

AFML-TR-71-44

AD 727 620

ADVANCED CHEMICAL MILLING PROCESSES

CHRISTIAN J. STAEBLER JR.
GRUMMAN AEROSPACE CORPORATION

TECHNICAL REPORT AFML-TR-71-44
March 1971

Approved for public release; distribution unlimited

FABRICATION BRANCH
MANUFACTURING TECHNOLOGY DIVISION
AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151



NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

| | |
|---------------------------------|---|
| APPROVED BY | |
| DATE | WHITE SECTION <input checked="" type="checkbox"/> |
| NO. | DIFF. SECTION <input type="checkbox"/> |
| UNAPPROVED | <input type="checkbox"/> |
| JUSTIFICATION | |
| BY | |
| DISTRIBUTION/AVAILABILITY CODES | |
| SEC. | AVAIL. and/or SPECIAL |
| A | |

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

ADVANCED CHEMICAL MILLING PROCESSES

Christian J. Staebler Jr.
Grumman Aerospace Corporation

Approved for public release; distribution unlimited

FOREWORD

This Final Technical Report covers all work performed under Contract F33(615)-69-C-1840 from 1 July 1969 through 31 December 1970. The report was released by the author in January 1971.

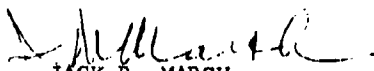
This contract with Grumman Aerospace Corporation, Bethpage, New York, was initiated under Manufacturing Methods Project 705-9, "Advanced Chemical Milling Processes." The work was administered under the technical direction of R. H. Coe, 1st/Lt., USAF, of the Fabrication Branch (LTF), Manufacturing Technology Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

The program was directed by Mr. Christian J. Staebler, Jr., Project Manager. The automated controls work was performed by Mr. K.T. Marshall and Mr. William Grauer of Advanced Materials and Processes Development. Other key personnel associated with the program were Miss Therese Kelleher, Mr. Guenther Baumann, Mr. Sidney Trink, and Mr. Olev Paul of Advanced Materials and Processes Development, and Mr. Lawrence Anton of Quality Control.

This project has been accomplished as part of the Air Force Manufacturing Methods Program, the primary objective of which is to develop, on a timely basis, manufacturing processes, techniques, and equipment for use in economical production of USAF materials and components.

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional manufacturing methods development on this or other subjects will be appreciated.

This technical report has been reviewed and is approved.



JACK R. MARSH

Chief, Fabrication Branch
Manufacturing Technology Division

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

| | | | |
|---|--|---|----------------------|
| 1. ORIGINATING ACTIVITY (Corporate author) Grumman Aerospace Corporation Bethpage, New York 11714 | | 2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED | |
| | | 2b. GROUP | |
| 3. REPORT TITLE Advanced Chemical Milling Processes | | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report (1 July 1969 to 31 December 1970) | | | |
| 5. AUTHOR(S) (First name, middle initial, last name) Staebler, Christian J., Jr. | | | |
| 6. REPORT DATE March 1971 | | 7a. TOTAL NO. OF PAGES 208 | 7b. NO. OF REFS 0 |
| 8a. CONTRACT OR GRANT NO. F-33(615)-69-C-184Q | | 8b. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-71-44 | |
| b. PROJECT NO. MMP 705-9 | | | |
| c. | | 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | |
| d. | | | |
| 10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited | | | |
| 11. SUPPLEMENTARY NOTES | | 12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson Air Force Base Dayton, Ohio 45433 | |
| 13. ABSTRACT The program objective was to improve the capability, reliability, and cost-effectiveness of chemical milling when applied to selected aerospace structural materials. A completely automated, centrifugal regeneration system for titanium hydrofluoric acid etchant was designed, fabricated, and tested. This system automatically analyzes the etchant, adds fresh acid, determines the titanium concentration, and activates a centrifuge which removes precipitated titanium and reclaims the etchant. A new, styrene-butadiene maskant was developed that gives excellent line definition on titanium substrates and that can be manufactured for about one-half the cost of commercially available maskants. The feasibility of using a laser-drilled, high-energy water jet to scribe chem-milling maskants was established. Optimum chem-milling/forming methodizing sequences were established that minimize distortion of titanium alloy detail parts. Sampling and analytical techniques were established for the major pollutants emitted by chem-milling operations. Air pollution control agencies and equipment manufacturers were surveyed. This is the Final Report for this program. | | | |

DD FORM 1 NOV 65 1473

205

UNCLASSIFIED

Security Classification

| KEY WORDS | LINK A | | LINK B | | LINK C | |
|-------------------------------|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Chemical Milling - Automation | | | | | | |
| Chemical Bath - Regeneration | | | | | | |
| Maskants - Scribing | | | | | | |
| Air Pollution | | | | | | |
| Methodizing | | | | | | |

ABSTRACT

The program objective was to improve the capability, reliability, and cost-effectiveness of chemical milling when applied to selected aerospace structural materials.

A completely automated, centrifugal regeneration system for titanium hydrofluoric acid etchant was designed, fabricated, and tested. This system automatically analyzes the etchant to determine the hydrofluoric acid concentration and adds fresh acid to maintain optimum concentration. The titanium section of the analyzer automatically determines the titanium concentration and activates a centrifuge which removes precipitated titanium, reclaims the hydrofluoric acid etchant, and maintains an optimum titanium concentration level.

A new, styrene-butadiene, chem-milling maskant was established that gives excellent line definition on titanium substrates. This maskant can be manufactured for about one-half the cost of commercially available maskants. A high-energy water jet was used to scribe chem-milling maskants. Photoresist pattern application methods, improved means of applying maskants, and more effective pin-hole detection techniques were also established.

Optimum chem-milling/forming methodizing sequences were established that minimize distortion of titanium alloy detail parts. The effectiveness of these optimized operational sequences was verified by determining tensile properties and hydrogen absorption values.

Sampling and analytical techniques were established for the major pollutants emitted by chem-milling operations. A survey of air pollution control agencies and equipment manufacturers provided information on existing pollution regulations, toxic effects, health hazards, and available control equipment.

CONTENTS

| <u>SECTION</u> | <u>PAGE</u> |
|--|-------------|
| I AUTOMATED CONTROL OF THE TITANIUM CHEM-MILL BATH TASK | 1 |
| 1. Approach | 1 |
| 2. Study Areas | 2 |
| 3. Automatic Analysis and Maintenance of Hydrofluoric Acid Concentration | 2 |
| 4. Automatic Analysis of Titanium Concentration | 24 |
| 5. Automatic Removal of Titanium from Etchant Solution and Reclamation of Hydrofluoric Acid | 43 |
| II MASKANT DEVELOPMENT TASK | 65 |
| 1. Approach | 65 |
| 2. Study Areas | 66 |
| 3. Improved Maskant Formulation | 66 |
| 4. Improved Application Techniques | 76 |
| 5. Photofabrication | 83 |
| 6. Automatic Scribing of Masked Parts | 94 |
| 7. Maskant Pinhole Detection Techniques | 115 |
| III METHODIZING OPTIMIZATION TASK | 125 |
| 1. Approach | 125 |
| 2. Study Areas | 126 |
| 3. Chemical Milling/Solution Heat Treating-Forming Evaluation ... | 129 |
| 4. Chemical Milling/Simultaneous Forming and Aging Evaluation ... | 144 |
| 5. Chemical Milling/One-Step Hot Forming Evaluation | 147 |
| 6. Chemical Milling/Heat Treating Evaluation | 150 |
| 7. Chemical Milling/Cold Working Evaluation | 157 |

CONTENTS (Cont)

| <u>SECTION</u> | <u>PAGE</u> |
|---|-------------|
| IV AIR POLLUTION TASK | 165 |
| 1. Approach | 165 |
| 2. Study Areas | 166 |
| 3. Sampling Techniques | 167 |
| 4. Analytical Techniques and Results | 173 |
| 5. Air Pollution Regulations for Chemical Milling Contaminants .. | 179 |
| 6. Air Pollution Control Equipment for Chemical Milling Operations | 188 |
| V CONCLUSIONS | 194 |

ILLUSTRATIONS

| <u>FIGURE</u> | | <u>PAGE</u> |
|---------------|---|-------------|
| 1 | Effect of Dissolved Fluorides on Equivalence Point Using Standard Titration | 3 |
| 2 | Masking Effect of Excess Hydrofluoric Acid on Equivalence Point (4.25N Bath Sample) | 4 |
| 3 | Masking Effect of Excess Hydrofluoric Acid on Equivalence Point (4.6N Bath Sample) | 5 |
| 4 | Automatic Analysis Time Intervals at Maximum Bath Depletion Rate for 10 Percent Hydrofluoric Acid Solution | 10 |
| 5 | Breadboarded Mechanical Section of Hydrogen Ion Analyzer ... | 12 |
| 6 | Reagent Overflow Burette and Teflon Valve | 15 |
| 7 | Timing Control Sequence for Mechanical Section of Hydro- fluoric Acid Analysis System | 16 |
| 8 | Component Mounting for Solid-State, Analog-Digital Circuit | 17 |
| 9 | Control Panel for Titanium Chem-Mill Analysis | 18 |
| 10 | Control Circuit Schematic for Automatic Hydrofluoric Acid Concentration System | 19 |
| 11 | Correlation of Electrical Signals with pH Readings | 21 |
| 12 | Analog Section of Hydrogen Ion Analysis System | 25 |
| 13 | Digital Section of Hydrogen Ion Analysis System | 27 |
| 14 | Stepper Switch Drive for Hydrofluoric Acid Concentration Control System | 29 |
| 15 | Automatic Hydrometer Specific Gravity Sensing System | 33 |
| 16 | Solid-State Regulator and Power Supply for Hydrofluoric Acid and Titanium Analyzers | 34 |
| 17 | Power System for Hydrofluoric Acid and Titanium Analyzers .. | 35 |
| 18 | Rack and Pinion for Moving Photocell/Light Unit | 38 |
| 19 | Titanium Concentration Analog Section | 39 |

ILLUSTRATIONS (Cont)

| <u>FIGURE</u> | | <u>PAGE</u> |
|---------------|---|-------------|
| 20 | Titanium Concentration Digital-to-Analog Converter | 41 |
| 21 | Centrifuge Remote Control Schematic | 45 |
| 22 | Precision Chemical Pumps | 47 |
| 23 | Centrifugal Regeneration Tanks and Control Room | 48 |
| 24 | Centrifugal Reclamation Piping Diagram | 49 |
| 25 | Centrifugal Precipitation and Feed Pumps | 52 |
| 26 | Sludge Collection System | 53 |
| 27 | Hydraulic Drive System and Other Mechanical Components of the Centrifuge | 54 |
| 28 | Timing and Discharge Systems for the Centrifuge | 55 |
| 29 | Effect of Centrifuging on Titanium Concentration in Hydrofluoric Acid Etchant | 56 |
| 30 | Comparison of Stoichiometric and Actual Amounts of Titanium Removed by Centrifuging | 58 |
| 31 | Pocket Chem-Milled in Test Panel Coated with Maskant No. 20 | 68 |
| 32 | Steps Chem-Milled in Test Panel Coated with Maskant No. 20 | 68 |
| 33 | Electrostatic Disc Atomizer for Maskant Application | 78 |
| 34 | Fully Automated Electrostatic Spray System for Maskant Application | 79 |
| 35 | Typical Chem-Milling Part Sizes for Fighter-Type Aircraft and Racking Arrangement for Electrostatic Spray System | 81 |
| 36 | Clear Polyvinyl Chloride (PVC) Photographic Tooling | 85 |
| 37 | Formed Aluminum Alloy Leading Edge Test Panel | 86 |
| 38 | Photographic Tool for Leading Edge Configuration | 87 |
| 39 | Water-Cooled, High-Pressure Mercury Vapor Lamps | 89 |

ILLUSTRATIONS (Cont)

| <u>FIGURE</u> | | <u>PAGE</u> |
|---------------|--|-------------|
| 40 | Formed Leading-Edge Part with Tooling and Ultraviolet Light Source | 95 |
| 41 | Formed Leading-Edge Part Inside Maskant Tool | 96 |
| 42 | Scribing Knife in Holding Fixture | 99 |
| 43 | X-Y Plotter Schematic | 100 |
| 44 | High-Pressure Water System | 102 |
| 45 | X-Y Plotter with Water-Jet Cutting Head | 103 |
| 46 | High-Pressure Water-Jet Cutting of Neoprene-Masked Panel | 104 |
| 47 | Experimental Nozzles Used in High-Energy Water-Jet Scribing of Chem-Mill Maskants | 106 |
| 48 | High-Energy Water-Jet Maskant Scribing Nozzle Fabricated by Two-Step Swaging Operation | 108 |
| 49 | Laser-Drilled Hole in 0.032-Inch-Thick Stainless Steel (500X Magnification) | 111 |
| 50 | Frames of High-Speed Film of Water-Jet Cutting | 112 |
| 51 | Maskant Scribing Cuts Made with 0.003-Inch-Diameter Laser-Drilled Nozzle | 113 |
| 52 | Spark Tester | 116 |
| 53 | Pinhole Detection-Voltage Gradient Method-Wet Sponge Probe | 117 |
| 54 | Pinhole Detection - Paths of Conductivity from Pinhole to Wand | 117 |
| 55 | Test Arrangement for Measuring Conductivity of Neoprene Maskant | 119 |
| 56 | Conductivity of 0.49 x 0.49 x 0.011-Inch Neoprene Sheet | 120 |
| 57 | Pinhole Detection-Voltage Gradient Method-Wand Detector | 121 |
| 58 | Titanium Engine Access Door Frame with Chem-Milled Pockets .. | 127 |

ILLUSTRATIONS (Cont)

| <u>FIGURE</u> | | <u>PAGE</u> |
|---------------|---|-------------|
| 59 | New 150-Ton U.S.I. - Clearing Hot Forming Press | 130 |
| 60 | Part Blank Being Positioned on Center Pin | 131 |
| 61 | Part Blank Being Positioned on End Pins | 131 |
| 62 | Formed Part Being Removed from Male Die | 132 |
| 63 | Formed Part Being Removed from the U.S.I. - Clearing Press | 132 |
| 64 | Forming Die | 133 |
| 65 | Solution Heat Treating Quenching Fixture | 138 |
| 66 | Cryogenic Quenching of Hot Formed Engine Access Door Frame in Liquid Nitrogen | 139 |
| 67 | TGS 5350 Tensile Specimen | 142 |
| 68 | Panels on Heat Treat Fixture Ready for Furnace Aging | 151 |
| 69 | Microsection of Ti-6Al-4V Panel Showing Alpha Layer (250X Magnification) | 156 |
| 70 | Microsection of Ti-6Al-4V Panel Showing No Alpha Layer (250X Magnification) | 156 |
| 71 | Typical Formed and Chem-Milled Curved Part | 159 |
| 72 | Experimental RDM-2239 Stretch Dil | 160 |
| 73 | Gas-Tight Syringes | 170 |
| 74 | Grab Sample Bottles | 170 |
| 75 | Polyethylene Bag with Portable Pump and Battery Used to Obtain Large-Volume Air Samples | 171 |
| 76 | Fritted Glass Bubblers with Flow Meters and Vacuum Pump | 171 |
| 77 | Perkin-Elmer Model 521 Infrared Spectrophotometer | 173 |
| 78 | Typical Gas Chromatographic Curve for Toluene | 174 |
| 79 | Perkin-Elmer Model 145D Chromatograph | 177 |
| 80 | Standard Curve for Colorimetric Fluoride Analysis | 180 |

TABLES

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|--|-------------|
| I | pH of Hydrofluoric Acid Samples Containing Titanium and Sodium Hydroxide | 7 |
| II | Maximum Part Size Etchable Per Volume of Solution | 9 |
| III | Hydrometer Rise Tests | 31 |
| IV | Calibration of System pH Meter | 59 |
| V | Comparison of pH Values of Titration Sample | 59 |
| VI | Comparison of Disposal Techniques for Waste, Fluoride-Containing Chem-Milling Solutions | 63 |
| VII | Evaluation of Maskant Formulations | 69 |
| VIII | Evaluation of Modified Maskant Formulations | 71 |
| IX | Characteristics of Maskant No. 20 | 73 |
| X | Composition of Chem-Mill Maskant Formulations | 74 |
| XI | Maskant Coating Thicknesses | 76 |
| XII | Physical Characteristics of Chem-Mill Maskants | 77 |
| XIII | Maskant Formula 27 Dilutions Tested Electrostatically | 80 |
| XIV | Material Usages for Electrostatic and Flow-Coating Techniques | 82 |
| XV | Effects of Curing Time and Temperature on Resistance of Photoresist Coatings to Attack by Hydrofluoric Acid | 91 |
| XVI | Effect of Ultraviolet Radiation Exposure Time on Resistance of Photoresist Coatings to Attack by Hydrofluoric Acid | 91 |
| XVII | Evaluation of Pretreatment Processes | 92 |
| XVIII | Adhesion and Etchant Resistance of Surface-Treated Titanium Alloy Test Panels | 93 |
| XIX | Cutting Force Data for Scribing Knives | 97 |
| XX | Summary of Water-Jet Maskant Scribing Tests | 105 |
| XXI | Summary of Fluorescent Dye Tests | 123 |

TABLES (Cont)

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|---|-------------|
| XXII | Test Procedures - Titanium Forming Study | 128 |
| XXIII | Solution Heat Treating/Forming - Methodizing Operations for Ti-6Al-4V and Ti-6Al-6V-2Sn Titanium Alloy Test Pieces | 135 |
| XXIV | Solution Heat Treating Forming Test Summary | 137 |
| XXV | Height Measurements of Chem-Milled Solution-Heat-Treat- Formed Ti-6Al-6V-2Sn Frames | 140 |
| XXVI | Height Measurements of Chem-Milled/Solution-Heat-Treat- Formed Ti-6Al-4V Frames | 141 |
| XXVII | Tensile Properties and Hydrogen Content of Titanium Alloy Engine Access Door Frames Processed by Various Methodizing Procedures | 143 |
| XXVIII | Simultaneous Forming and Aging/Chemical Milling Methodizing Operations for Ti-6Al-4V and Ti-6Al-6V-2Sn Titanium Alloy Test Pieces | 145 |
| XXIX | Height Measurements of Chem-Milled/Simultaneously Formed and Aged Titanium Alloy Frames | 146 |
| XXX | Chemical Milling/Hot Forming Methodizing Operations | 148 |
| XXXI | Height Measurements of Chem-Milled/One-Step Hot Formed Titanium Alloy Frames | 149 |
| XXXII | Chemical Milling/Heat Treating Summary | 152 |
| XXXIII | Height Measurements of Chem-Milled/Heat Treated Titanium Panels | 153 |
| XXXIV | Processing History and Tensile Properties of Titanium Alloy Panels Subjected to Various Chemical Milling/Heat Treating Operations | 158 |
| XXXV | Chemical Milling/Roll Forming/Incremental Brake Forming Methodizing Operations for Ti-8Al-1Mo-1V Titanium Alloy Sheet | 161 |
| XXXVI | Radius Measurements on Ti-8Al-1Mo-1V Titanium Alloy Parts Roll Formed and Incrementally Brake Formed at Room Temperature and then Chem-Milled | 163 |

TABLES (Cont)

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|--|-------------|
| XXXVII | Geographical Location of Major Chemical Milling Contractors and Subcontractors | 167 |
| XXXVIII | Air Pollutants from Chemical Milling Processes | 168 |
| XXXIX | Ambient Air Quality Standards | 186 |
| XXXX | Comparision of Incineration Systems | 192 |

INTRODUCTION

PURPOSE

The purpose of this project was to improve chemical milling processes and associated equipment that employ straight chemical energies.

OBJECTIVE

The objective of the program was achieved by advancing selected chemical milling parameters, with particular emphasis on the control elements for more effective and precise fabrication at lower costs. The program was directed towards upgrading and developing time-phased tasks in the following four categories: Automated Control of the Titanium Chemical Milling Bath, Maskant Development, Methodizing Optimization, and Air Pollution.

The data generated during this program will contribute to more efficient procedural techniques. A completely automated control system for maintaining an optimum titanium chem-milling solution was designed, fabricated, and evaluated. This system involves automatic determination of hydrofluoric acid and titanium concentrations, automatic precipitation and removal of titanium, and automatic addition of hydrofluoric acid to maintain desired bath normality. A new chem-mill maskant and an improved means of applying maskants were established that reduced maskant application costs. Photoresist techniques were established that make it possible to chem-mill the interior of parts having a bend radius less than two inches. Development of a high-energy, water jet cutting technique for chem-mill maskants established the feasibility of automating maskant scribing. Methodizing sequences for titanium alloy detail parts that involve chemical milling, hot forming, and heat treating operations were optimized to minimize part distortion. New sampling and analytical techniques for chem-milling pollutants were developed that make it possible for chem-milling contractors to comply with air pollution regulations.

SECTION 1

AUTOMATED CONTROL OF THE TITANIUM CHEM-MILL BATH TASK

1. APPROACH

The automation task was directed primarily toward applying current technologies to reduce chem-mill production costs. An automatic analyzer was designed, fabricated, and evaluated for control of the titanium chem-mill bath and related centrifuge reclamation equipment. The conclusions reached as a result of this study are:

- A new analytical technique, which involves the use of hydrofluoric acid of known normality to reduce metallic interference, was developed that makes it possible to simply and automatically determine the hydrofluoric acid concentration in titanium chem-milling etchants.
- A hydrometric analytical technique was developed to determine the titanium concentration in hydrofluoric acid-based, chem-milling etchants. This technique, which is based on changes in etchant specific gravity caused by varying amounts of dissolved titanium, facilitated the automation of the centrifugal regeneration process for titanium chem-milling etchants.
- An automatic analyzer that was designed and built by Grumman can be effectively used to determine hydrofluoric acid and titanium concentrations and to provide the signals for initiation of the centrifugal titanium removal cycle and addition of make-up hydrofluoric acid.
- The ten percent hydrofluoric acid etchant used to chem-mill titanium can be automatically reclaimed by precipitating the dissolved titanium with potassium fluoride and removing it as potassium fluotitanate sludge in a centrifuge operation.
- An automatic centrifugal regeneration process was developed that not only alleviates the fluoride waste disposal problem but also reclaims 50 percent of the hydrofluoric acid etchant. This process eliminates the need for manual recharging of the etchant tanks, increases production rates, and improves part dimensional tolerances by maintaining etchant bath parameters at optimum levels. Use of the automated, centrifugal regeneration process would reduce waste solution disposal costs by 50 to 65 percent below that for vendor removal costs.

2. STUDY AREAS

The task of developing the automated system for control of the titanium chem-mill bath consisted of the following technical efforts:

- Automatic analysis and maintenance of hydrofluoric acid concentration
- Automatic analysis of titanium concentration
- Automatic removal of titanium from the bath solution and reclamation of hydrofluoric acid.

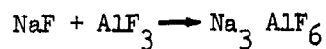
3. AUTOMATIC ANALYSIS AND MAINTENANCE OF HYDROFLUORIC ACID CONCENTRATION

a. Standardization of Laboratory Procedure for Analysis of Hydrofluoric Acid Concentration

The first requirement for design of the hydrofluoric acid section of the automatic analyzer was to establish a simple and reproducible analytical procedure capable of responding to electronic interpretation. Direct neutralization of hydrofluoric acid with 0.1 normal sodium hydroxide was found to be unsatisfactory (see titration curves in Figure 1. In the absence of dissolved titanium alloy, neutralization of hydrofluoric acid etchant with sodium hydroxide will yield a sharp potential difference at the equivalence point. When titanium alloy is added, it reacts with the etchant to form the metallic fluorides of the alloy constituents. It is the interference of these metallic fluorides that inhibits the establishment of a sharp equivalence point during the acid-base titration. The competing reaction is the formation of metallic oxyfluorides and metallic oxides.

In order to eliminate metallic interference without incorporating precipitation and filtration steps in the analytical procedure, several complexing agents were examined -- potassium fluoride, ethylene diamine tetracetic acid, oxalic acid, and a known excess of hydrofluoric acid. The greatest differential at the equivalence point was obtained with a known excess of hydrofluoric acid. The improved titration curves obtained with this modification are shown in Figures 2 and 3.

It is known that sodium fluoride will react with metallic fluorides to form fluoroanions as shown below:



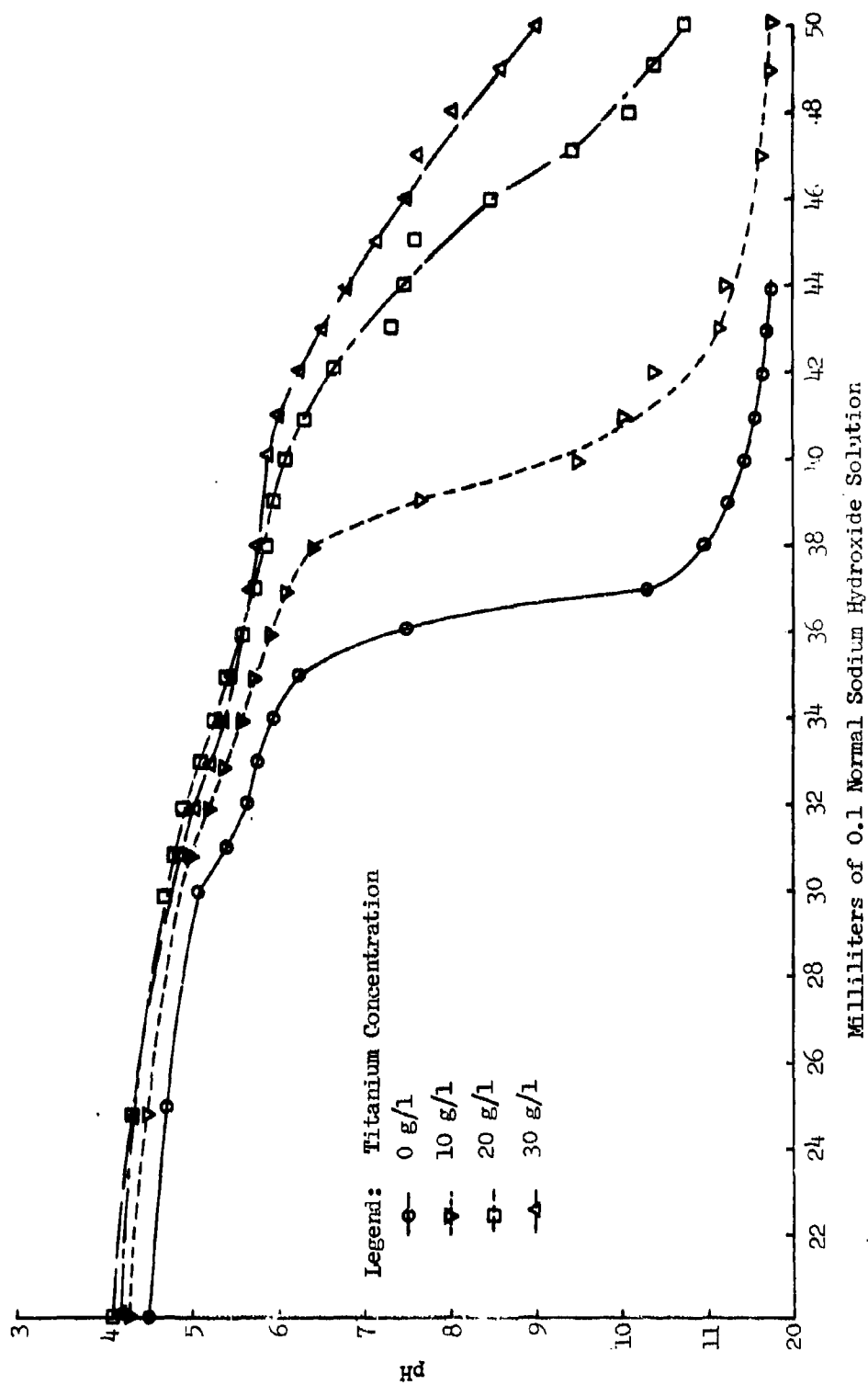


Figure 1 Effect of Dissolved Fluorides on Equivalence Point Using Standard Titration.

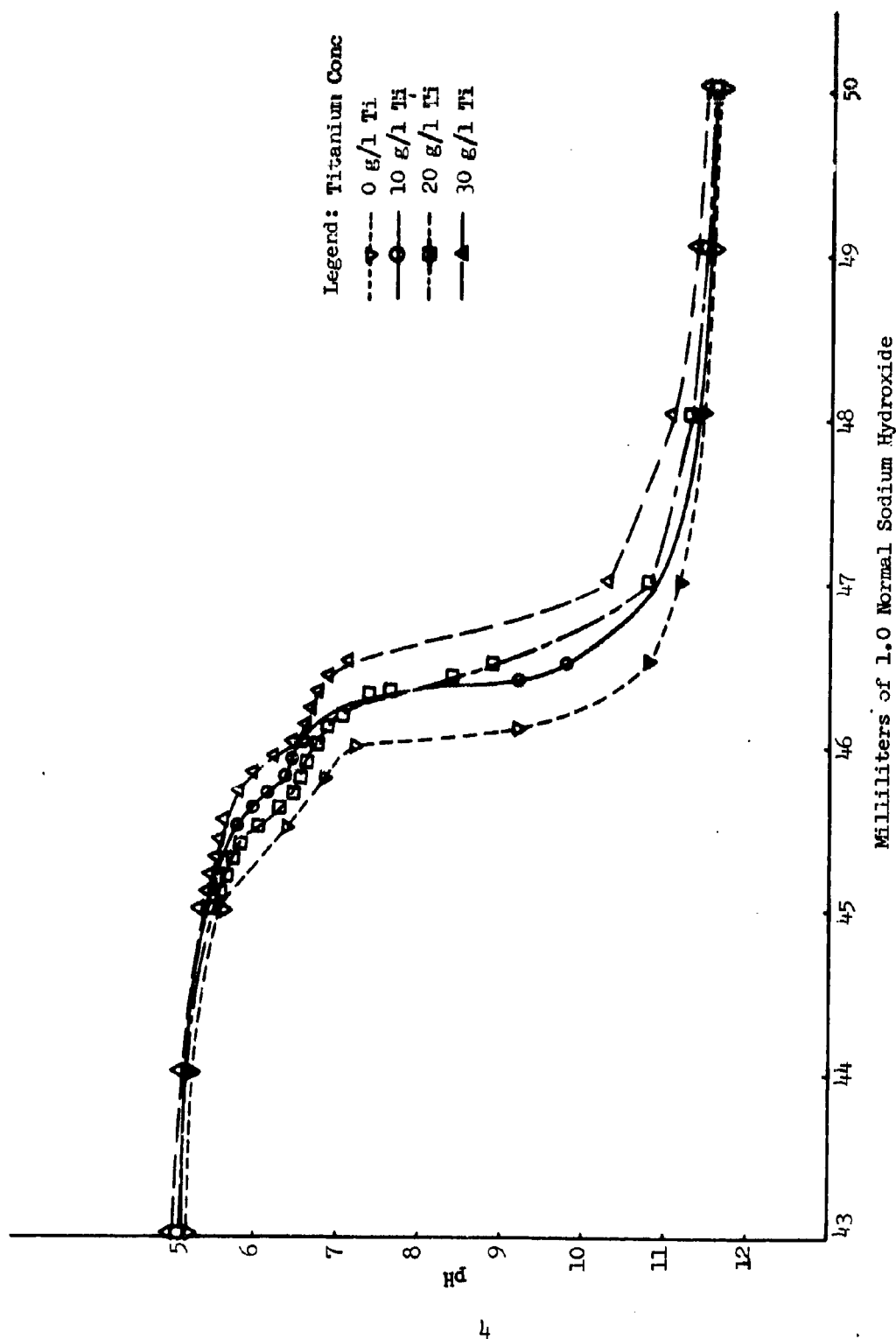


Figure 2 Masking Effect of Excess Hydrofluoric Acid
on Equivalence Point (4.25 N Bath Sample)

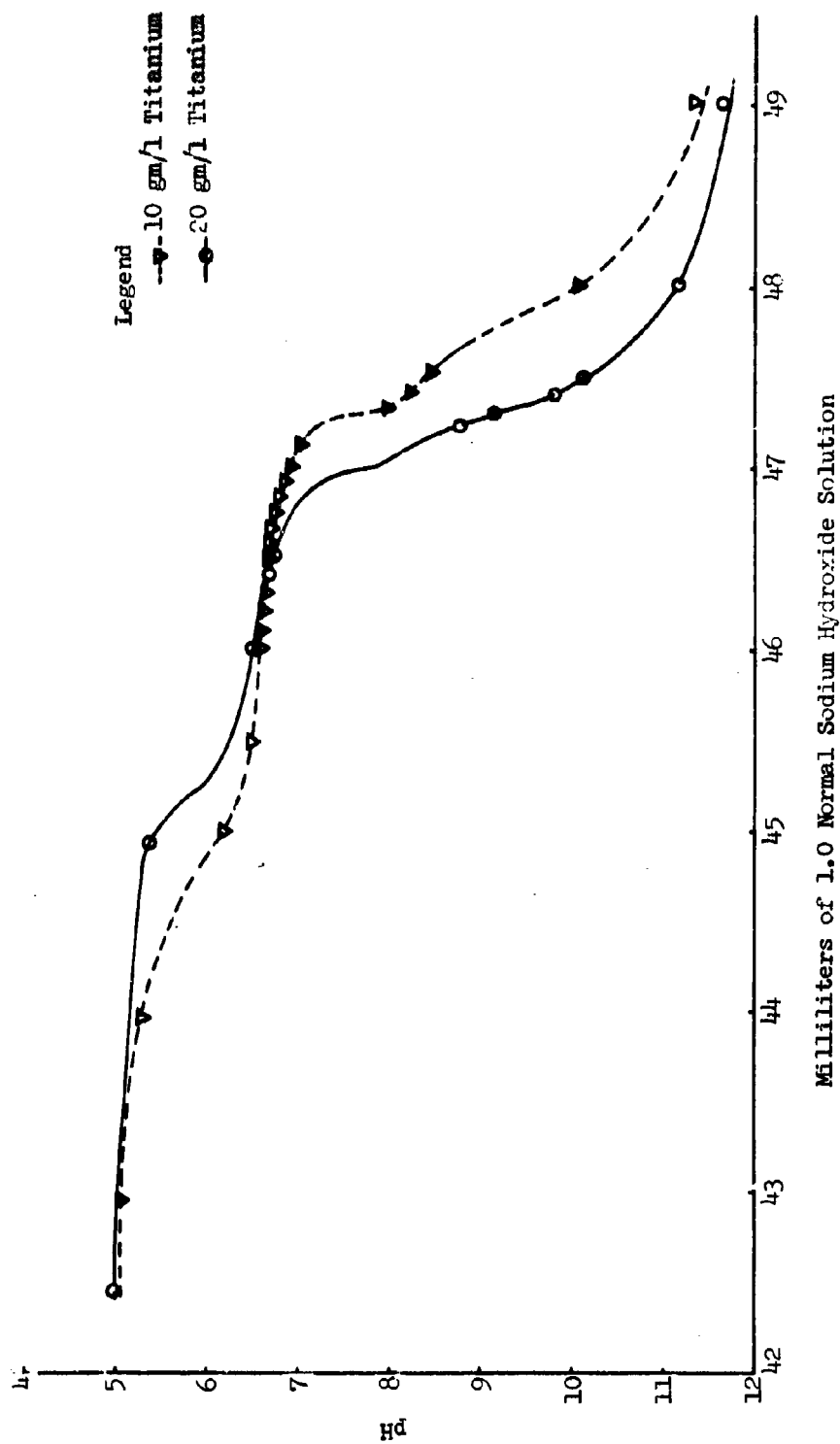
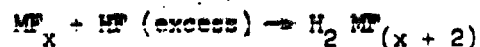


Figure 3 Masking Effect of Excess Hydrofluoric Acid on Equivalence Point (4.6 M Bath Sample)

Based on this evidence the probable chemical reactions are:



The large pH differential facilitates the use of an automatic analysis system in which an electronic signal from a pH meter can be used directly. When 47 milliliters of 1.0 normal sodium hydroxide plus excess hydrofluoric acid of a known normality are added to a 4.25 normal etchant solution, pH values of 10.8 to 10.9 are obtained for solutions with 10 and 20 grams per liter of titanium (Figure 2). When the same procedure is used with a 4.6 normal etchant, pH values of 7.8 and 6.8 are obtained (Figure 3).

For this laboratory study the following analytical procedure was used:

- 10 milliliters of 4.25 normal hydrofluoric acid and 10 milliliters of a 1:10 dilution of etchant sample were added to a 250-milliliter beaker
- Total volume was brought to 100 milliliters with distilled water
- Magnetic stirrer was engaged
- Total acid was titrated with 1.0 normal sodium hydroxide as shown in Figure 2.

Tests were conducted to reduce the time to carry out the analytical procedure to a level suitable for automatic analysis; bulk additions of 1.0 N sodium hydroxide were added to several samples whose pH levels were then determined. Data obtained are presented in Table I.

TABLE I

pH OF HYDROFLUORIC ACID SAMPLES CONTAINING TITANIUM AND SODIUM HYDROXIDE

| HYDROFLUORIC ACID CONCENTRATION (normality) | TITANIUM CONCENTRATION (grams/liter) | VOLUME OF 1.0 N NaOH (ml.) | pH | |
|---|---|-------------------------------------|------|-----------|
| | | | Bulk | Titration |
| 4.40 | None | 46.4 | 6.70 | 6.75 |
| 4.10 | None | 46.4 | 7.00 | 6.95 |
| 3.80 | None | 46.4 | 9.50 | 9.30 |
| 3.40 | None | 46.4 | 10.2 | 10.35 |
| 4.25 | 10 | 46.4 | 8.40 | 8.60 |
| 4.25 | 20 | 46.4 | 8.00 | 8.40 |

pH values for the bulk additions correspond satisfactorily to those for the standard titration method. Rapid analysis can be achieved, therefore, by simply adding a specific volume of titrant to a specific volume of bath sample, mixing, and monitoring the change in pH.

The analysis sequence of operations for the bulk additions is as follows:

- Add 89 milliliters of distilled water to a mixing beaker
- Add 46.75 milliliters of 1 N NaOH from a burette to the mixing beaker
- Add 10 milliliters of 4.25 N hydrofluoric acid to the mixing beaker
- Add one milliliter of etchant to the mixing beaker
- Record pH of solution in beaker.

Use of the above bulk additions and bath samples containing zero to 30 grams per liter of titanium will give a pH range of 8.3 to 10.9 (see Figure 2).

b. Automatic Analysis of Hydrofluoric Acid Concentration

The data generated by the bulk analysis sequence was used in the design of an automated control system for hydrofluoric acid etchants. The bulk addition procedure was modified by increasing the reagent volumes by a factor of five to make it easier to design the reagent burettes. The sodium hydroxide volume was increased by a factor of two and the solution normality was increased from 1.0 N to 2.5 N. The analysis sequence of operations for the modified bulk addition procedure was as follows:

- Add 445 milliliters of distilled water to a mixing beaker
- Add 93.5 milliliters of 2.5 N NaOH
- Add 50 milliliters of 4.25 N HF
- Add 5 milliliters of sample

Addition of the above solution volumes together with a bath sample normality of 4.25 N will give a pH range of 8.3 to 10.9. Since these values are considered acceptable bath control limits, concentrated hydrofluoric acid does not have to be added to replenish the bath until the pH level rises above 10.9.

The error band was further reduced by maintaining the titanium concentration between 10-20 grams per liter; this is accomplished by the titanium analyzer. Practical control limits can be maintained to an accuracy of plus or minus 0.2 N. Based on the maximum input of titanium to the bath and the normality control limits chosen, an analysis time interval was established. For example, a three-gram-per-liter increase in titanium concentration is required to produce a 0.2 N decrease in bath concentration. The analysis time interval to be chosen, therefore, should be the maximum rate at which the bath titanium concentration can increase to three grams per liter.

The pilot tank facility used for all testing has a capacity of 1,500 gallons. It was found that excess heat was not evolved when parts having an equivalent area up to 25 square feet were chem-milled in 1,000 gallons of etchant for 75 minutes. Cooling with cold tap water could be used when larger work areas are involved. Test results are presented in Table II.

TABLE II

MAXIMUM PART SIZE ETCHABLE PER VOLUME OF SOLUTION

| SIZE SAMPLE EXPOSED TO 25 LITERS OF ETCHANT (sq. in.) | SIZE EQUIVA- LENCE USING 1,000 GAL. OF ETCHANT (sq. ft.) | TEMP. RISE (°C/min) | AVERAGE ETCH RATE (mil/min) | TIME (min) | REMARKS |
|---|--|---------------------------|--------------------------------------|---------------|------------|
| 52.5 | 55 | 1°/2 | 2.0 | 40 | No Cooling |
| 37.8 | 40 | 1°/10 | 1.3 | 65 | No Cooling |
| 23.6 | 25 | 1°/15 | 1.2 | 75 | No Cooling |

The time period in which three grams per liter of titanium (density of 0.17 pounds per cubic inch) should be added to 1,000 gallons (or 3,783 liters) of etchant in which a 25-square-foot part is being etched at a rate of 0.001 inch per minute can be calculated as follows:

$$\frac{(3,783 \text{ liters}) (3 \text{ gms/liter})}{(25 \text{ sq ft})(144 \text{ sq in/sq ft})(0.001 \text{ in/min})(0.17 \text{ lbs/cu in})} =$$

$$\frac{25 \text{ lbs titanium}}{0.612 \text{ lbs/min}} = 40 \text{ minutes}$$

The 40-minute time interval, then, is the maximum time period in which a 10-percent hydrofluoric acid solution becomes depleted (Figure 4).

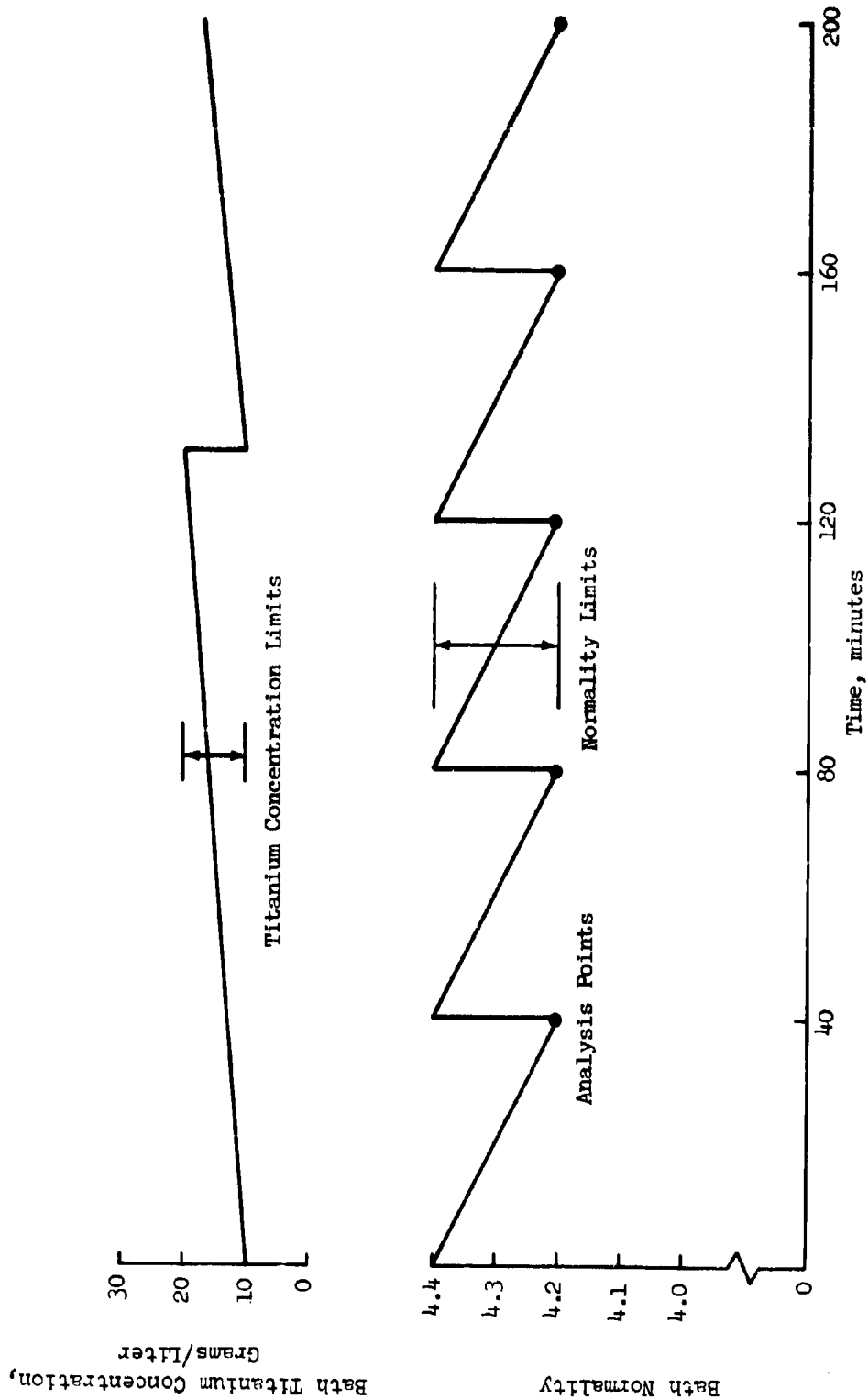
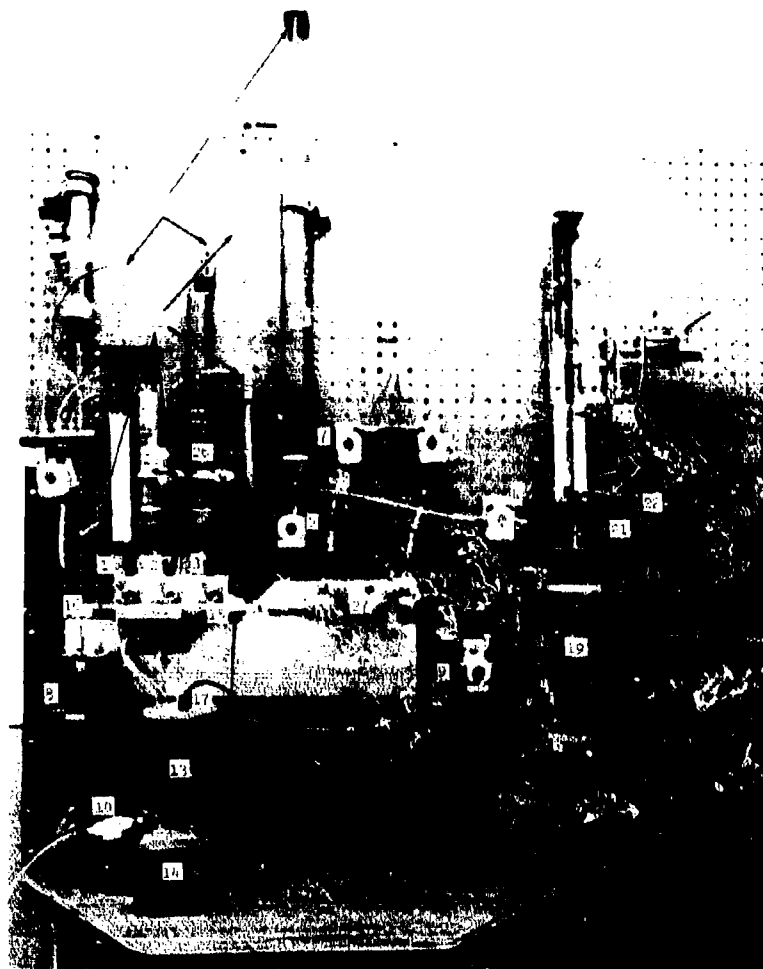


Figure 4 Automatic Analysis Time Intervals at Maximum Bath Depletion Rate for 10 Percent Hydrofluoric Acid Solution

c. Design of Automated Control System for Hydrofluoric and Concentration

- (1) Mechanical - The mechanical portion of the hydrofluoric acid analysis system consists of a series of accurate overflow burettes that measure the volumes of the analysis reagents and the bath sample. The burettes are controlled by solenoids and a rack-and-spur gear arrangement. Accuracy of the burettes is maintained by raising or lowering a displacement rod. The breadboarded system is shown in Figure 5. The polyvinyl chloride (PVC) overflow burette (24) draws 445 milliliters of distilled water from a supply tank. Solenoid-actuated valves (4 and 5) control filling and draining of the burette to the PVC mixing beaker (13). After the distilled flushing water has been drained into the mixing beaker, the magnetic stirrer (14) is activated. The Teflon burette (1) and the PVC burettes (25 and 26) are then filled with five milliliters of hydrofluoric bath etchant, 50 milliliters of 4.25 N hydrofluoric acid, and 94 milliliters of 2.5 N sodium hydroxide, respectively. This is accomplished by the horizontally positioned air cylinder (27) which powers a rack (15) that is meshed with three pinion gears. Each gear actuates a three-position rotary valve on the base of each burette (1, 2, and 3). When air is supplied to the piston cylinder, the rack extends to its extreme left position where it remains until a preset timing cycle is completed. During this cycle regulated flow of 2.5 N sodium hydroxide and 4.25 N hydrofluoric acid from gravity supply tanks and pressure flow of hydrofluoric acid from the etchant tank refill the burettes. Timing is adjusted so that a small amount of each fluid overflows from each burette (12). The quantity of fluid in each burette is controlled by adjusting the height of immersed rods (18). An air cylinder (8) is then actuated so that the rising piston engages the stop (16) on the rack, thereby preventing full return of the rack to the right. In reaching this position, the rack has turned the pinion gears which, in turn, rotates each three-way valve to the "OFF" position. Actuation of the air cylinder (8) withdraws the piston which allows the rack to complete its stroke to the right. This rotates the burette valves to the "DUMP" position which allows the fluids in the burettes to flow into the mixing beaker (13). After the fluids have been mixed for 30 seconds, the solution is analyzed for hydrogen ion content by pH meter probes (17). The resultant signal is fed into a pH meter which determines whether the concentration of the etchant bath should be increased. If the etchant bath needs more hydrofluoric acid, the pH meter sends a signal to a timer which starts a pump that replenishes the hydrofluoric acid at a predetermined rate for ten



- | | |
|--|--|
| 1. Teflon Rotary Valve for Sampling Burette | 15. Rack and Pinion Gears |
| 2. Teflon Rotary Valve for Maskant Burette | 16. Stop |
| 3. Teflon Rotary Valve for NaOH Burette | 17. pH Probes |
| 4. Solenoid Valve for Water Burette | 18. Calibration Rods |
| 5. Solenoid Valve for Dumping Water | 19. Hydrometer Overflow Cylinder |
| 6. Air Solenoid Valve to Actuate Cylinder | 20. Surge Tank |
| 7. Air Solenoid Valve to Return Cylinder | 21. Hydrometer |
| 8. Air Cylinder for Indent | 22. Photo-electric Cell and Light |
| 9. Solenoid Valve for Water Flushing Beaker | 23. Sensing Rack and Pinon with Gear Motor Drive |
| 10. Solenoid Valve to Empty Beaker | 24. PVC Water Burette |
| 11. Air Solenoid Valve to Blow Down Burettes | 25. PVC HF Masking Acid Burette |
| 12. Overflows from Burettes | 26. PVC NaOH Burette |
| 13. Mixing Beaker | 27. Air Cylinder |
| 14. Magnetic Stirrer | |

Figure 5 Breadboarded Mechanical Section of Hydrogen Ion Analyzer

minutes. When the analysis has been completed, the PVC dump valve (16) on the bottom of the mixing beaker is opened to allow the solution to drain. The polished conical bottom of the mixing beaker retains only a minimum of residue. A flushing water cycle rinses the mixing beaker. The dump valve is then closed to allow water to fill the beaker so that the probes are continuously immersed in water between cycles.

During checking of the prototype mechanical section of the Hydrogen Ion analyzer for liquid measurement error, it was found that the as-manufactured, three-way, commercial valves installed in the system did not perform satisfactorily. Although these valves were designed to direct liquid flow in any of three directions, no provision was made for an "off" or null position. An attempt to establish an "off" section between the flow parts was not successful. In addition, the valves were manufactured to such large tolerances that considerable leakage occurred after several cycles. New Teflon valves (Figure 6) were designed and fabricated that have a maximum amount of "off" arc between the inlet and outlet positions of the rotating valve stem and reduced clearance between the stem and valve body such that the "O"-ring seals are compressed to the maximum degree possible when the stem is installed in the reamed hole of the valve body. Tests with water showed an adequate arc of rotation in the "off" position and no leakage. The rate of flow can be adjusted by either changing the diameter of the flow hole in the valve stem or the degree of rotation of the stem. A schematic diagram of the mechanical section of the hydrofluoric acid analysis system showing the solenoid-control-valve timing sequence is shown in Figure 7.

- (2) Electrical - The electrical circuitry that was designed to control hydrofluoric acid concentration consists of two sections -- a control circuit to sequence the titration procedure and a solid state analog-digital circuit to determine when addition of hydrofluoric acid is needed. The analog-digital section was mounted on printed circuit boards and installed on a standard 19-inch rack (Figure 8). The control panel is shown in Figure 9.

The control circuit shown in Figure 10 contains a programmed stepping switch that sequences the necessary operations. This switch has 18 steps and 20 independent limit switches. Cams placed along the drum of the unit determine which switches are closed for each of the 18 positions of the drum. The stepping switch cycle is initiated by timer 2TR which determines how often an analysis is made. At the end of the cycle, the stepping switch stops and is restarted upon command from timer 2TR. During the analysis cycle, the following sequence of operations takes place:

- Water in the mixing beaker that is used to keep the pH probes wet is drained, under control of limit switch 7CS. Concurrently, limit switch 2CS permits the reactants to flow into the calibrated burettes.
- Limit switch 5CS permits the transfer of distilled water from a burette to the mixing beaker.
- Limit switch 6CS adds the remaining reactants to the mixing beaker and activates the magnetic mixer.
- Limit switch 10CS turns off the circulating pump of the titanium concentration hydrometer. This is done to allow the hydrometer to settle.
- Limit switch 9CS energizes the pH meter and the analog-digital circuit, which determines when to add concentrated hydrofluoric acid.
- After a sufficient time period has elapsed for operation of the analog-digital circuit, limit switches 7CS and 8CS initiate a drain-rinse cycle for the mixing beaker. Limit switch 8CS then fills the mixing beaker with water to keep the probes wet.
- Limit switch 11CS deactivates the stepping switch at the end of the cycle.

In the event that the emergency switch is depressed, the centrifuge will be stopped, a buzzer inside the control room and a bell outside the control room will sound, and a lamp will flash on and off.

The analog-digital section determines when concentrated hydrofluoric acid should be added to the bath. Its operation is described in the following paragraphs.

When all reactants are in the mixing beaker, the output of the pH meter is interrogated. The pH meter output, which ranges from -350 mv to +350 mv, corresponding to a zero-to-14 pH range (Figure 11), is fed to differential amplifier A (11) (Figure 12). The signal is amplified by amplifier A (12) so that the digital readout voltmeter, which has a full scale of 200 mv, will read pH directly. The output of amplifier A (12) is also channeled to a comparator circuit consisting of amplifier A (22). The current direction at the inverting input of amplifier A (22) is determined by the voltages at BB and BD of Board 2 as well as the ratio of the two input resistances. The voltage of BB represents the manual

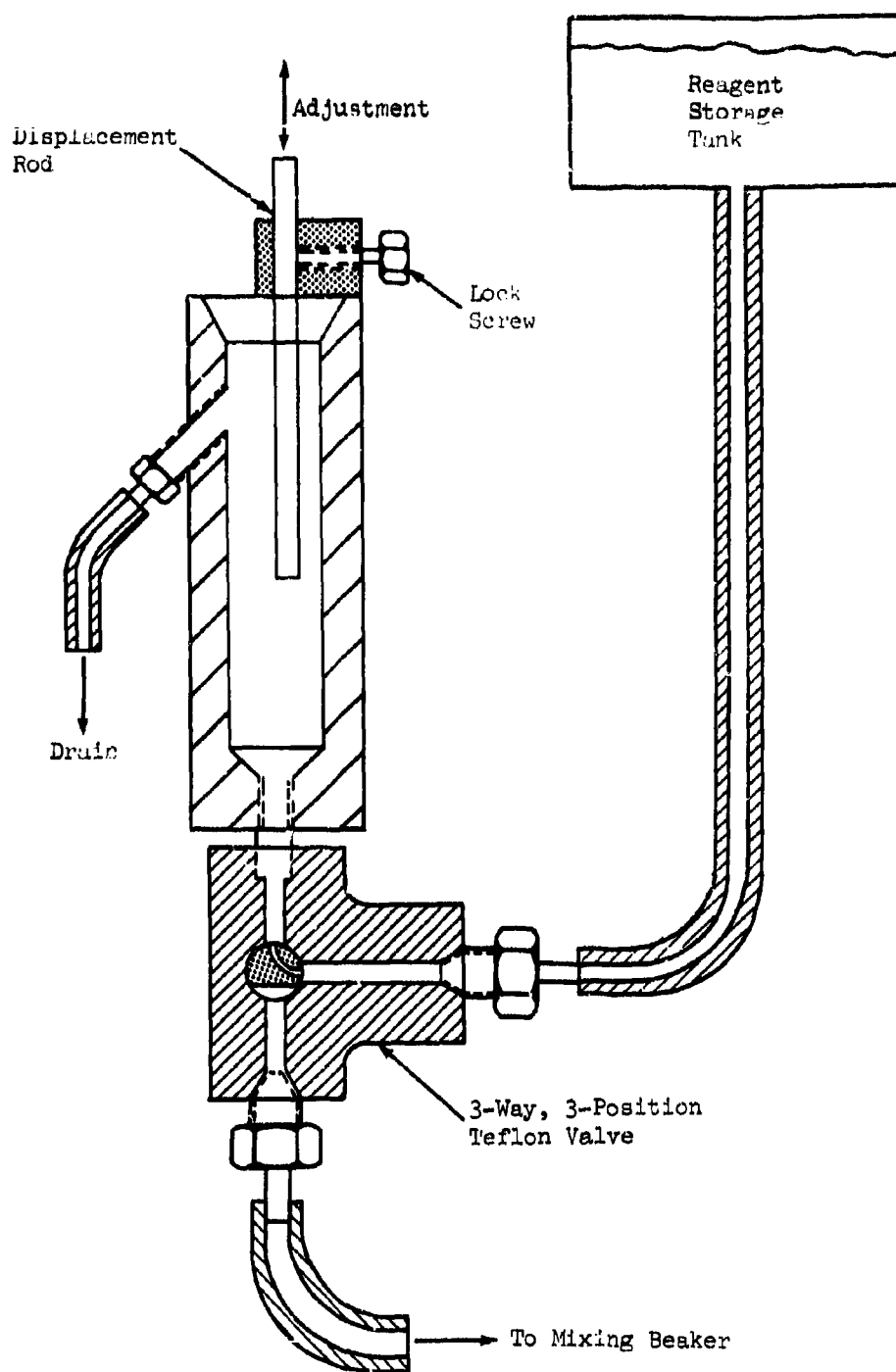


Figure 6 Reagent Overflow Burette and Teflon Valve

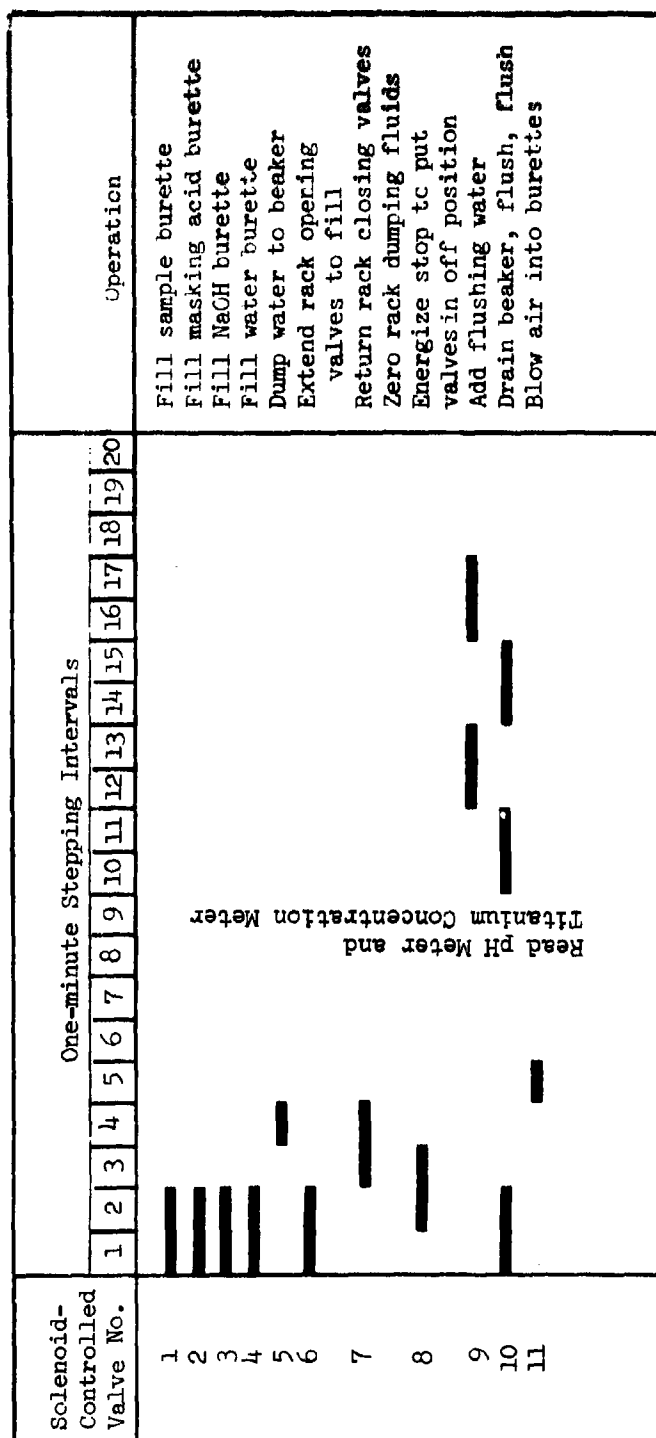


Figure 7 Timing Control Sequence for Mechanical Section of
Hydrofluoric Acid Analysis System

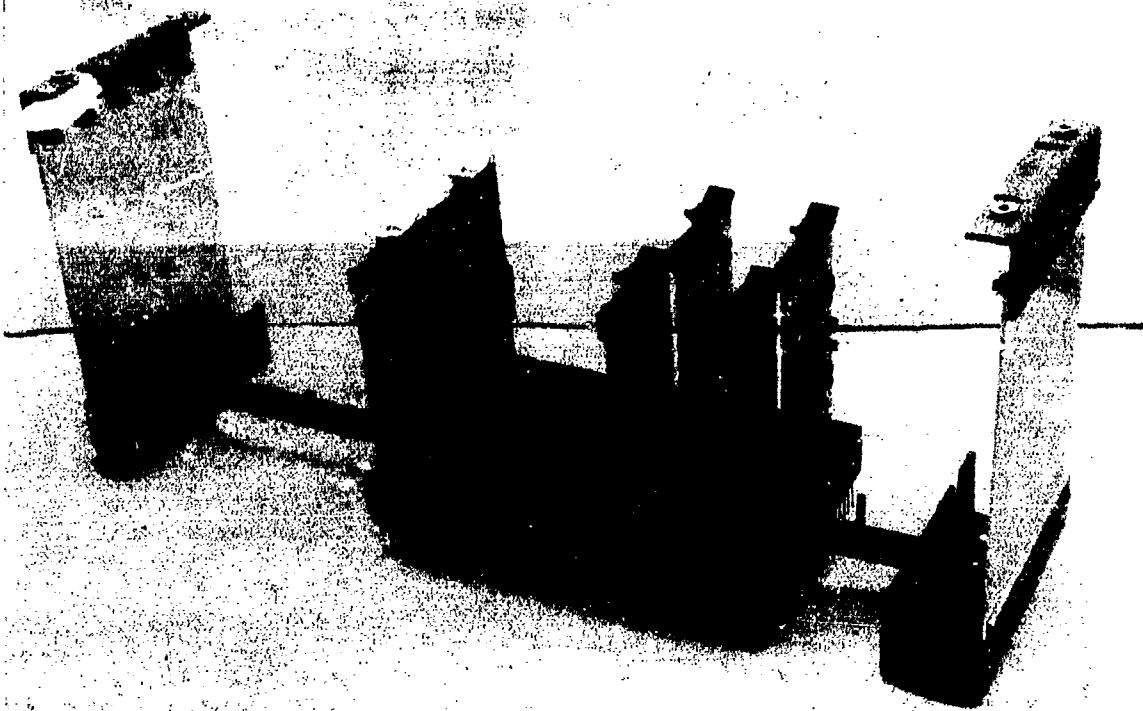


Figure 8 Component Mounting for Solid-State, Analog-Digital Circuit

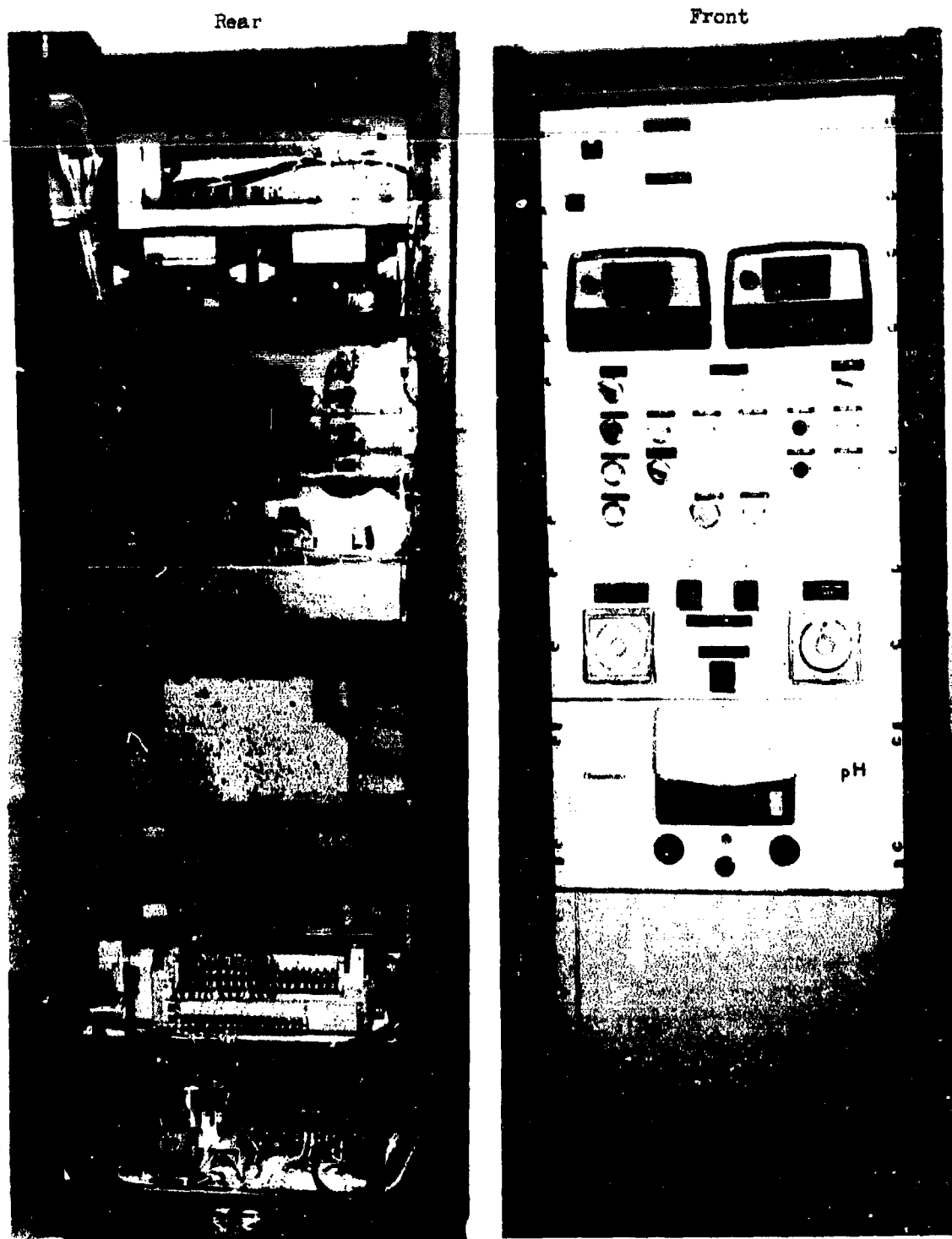
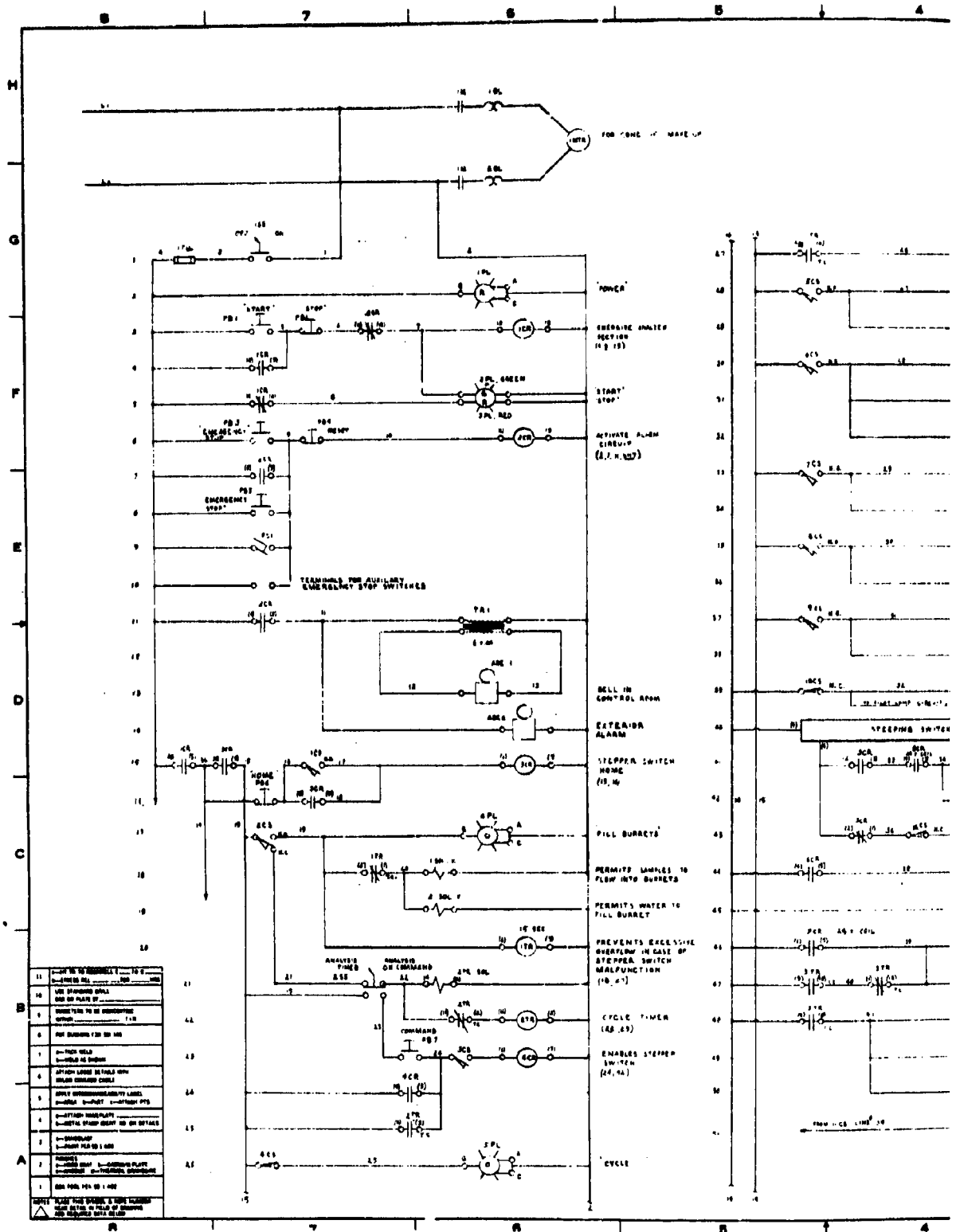


Figure 9 Control Panel for Uranium Chem-Mill Analysis.



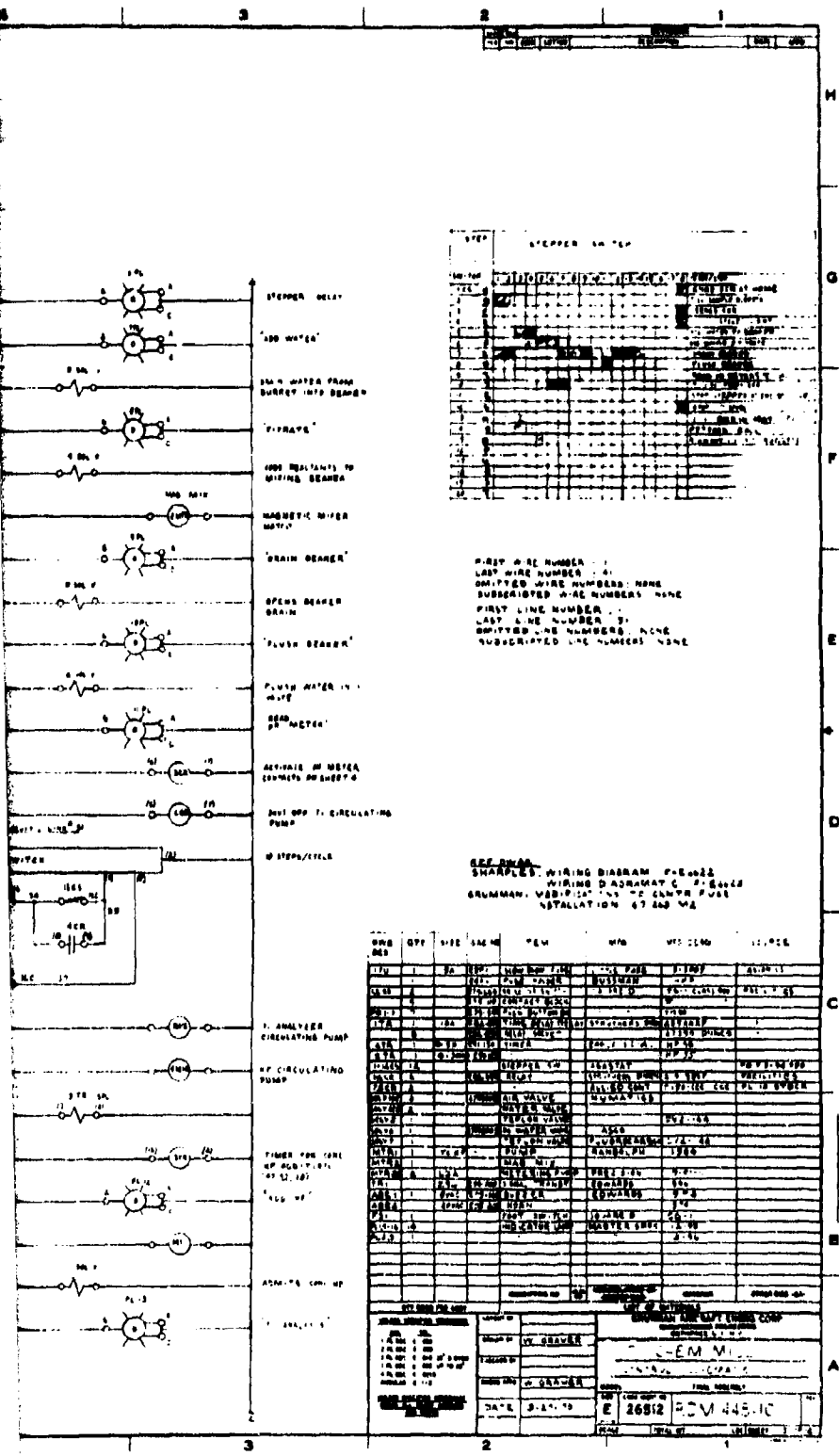
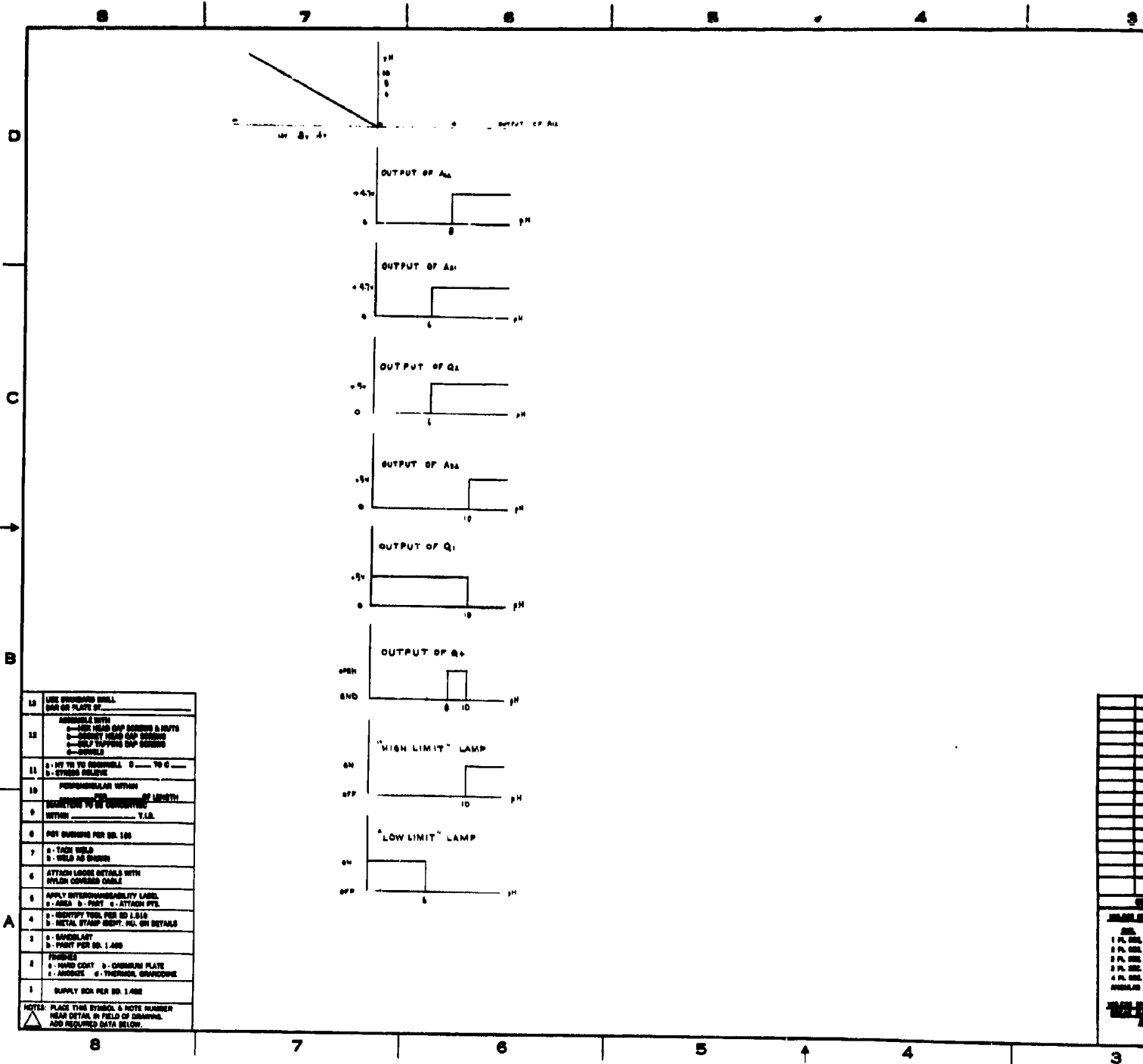


Figure 10 Control Circuit Schematic for Automatic Hydrofluoric Acid Concentration System

B

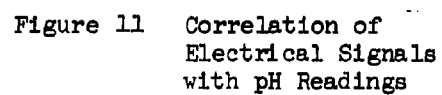


1. USE STANDARD BELL BAR OR PLATE OF _____
2. ASSEMBLE WITH _____
 a. ADD HEAD GAP SENSING & MOUNT
 b. ADD HEAD GAP SENSING
 c. ADD TAPPING GAP SENSING
 d. SCALE
3. a. SET TO TO REMOVAL 0 TO 0
 b. STAINLESS STEEL
4. PERMANENTLY MOUNTED
 a. IDENTIFY YIELD, PER ED L.1.1.1
 b. IDENTIFY TO BE CONSIDERED
 WITHIN _____ T.I.R.
5. FOR DRAWING PER ED. 1.1.1
6. a. TACK WELD
 b. WELD AS SHOWN
7. ATTACH LOCKS DETAILS WITH NYLON COVERED CABLE
8. APPLY INTERFEROMETER LABEL
 a. AREA b. PART c. ATTACH PTE
9. a. IDENTIFY YIELD, PER ED L.1.1.1
 b. METAL STAMP IDENT. HX. ON DETAILS
10. a. SOLDER/ANT
 b. POINT PER ED. 1.1.1.1
11. FINISHES
 a. HARD COAT b. CHROMIUM PLATE
 c. ANODIZE d. THERMAL SHROUDING
12. SUPPLY BOX PER ED. 1.1.1.1

NOTES: PLACE THIS SYMBOL & NOTE NUMBER NEAR DETAIL IN FIELD OF DRAWING. ADD REQUIRED DATA BELOW.

A

| | |
|----|-------------|
| 1 | PL. 1.1.1.1 |
| 2 | PL. 1.1.1.1 |
| 3 | PL. 1.1.1.1 |
| 4 | PL. 1.1.1.1 |
| 5 | PL. 1.1.1.1 |
| 6 | PL. 1.1.1.1 |
| 7 | PL. 1.1.1.1 |
| 8 | PL. 1.1.1.1 |
| 9 | PL. 1.1.1.1 |
| 10 | PL. 1.1.1.1 |
| 11 | PL. 1.1.1.1 |
| 12 | PL. 1.1.1.1 |



input voltage from the pH set point potentiometer. Amplifier A (21) is used to remove the loading effect that the one meg-ohm resistor would have on the potentiometer, if amplifier A (21) were not present. Amplifier A (21) also makes it possible to use a wide range of resistor values on the input of amplifier A (22).

The output of amplifier A (22) (Figure 12) will be either +4.7 volts or -0.7 volt. These two values are determined by the Zener breakdown voltage and the forward voltage drop of the diode. The Zener voltage level of 4.7 volts was chosen to make the output compatible with that of the digital logic circuitry. A voltage of 4.7 volts indicates that addition of concentrated hydrofluoric acid is required.

Amplifier A (31) and A (32) are comparators that determine when the pH value of the sample has exceeded the normal operating range. This situation indicates that a problem exists in controlling the bath and the circuit inhibits further additions of concentrated hydrofluoric acid to the bath. A lamp is energized to indicate the situation.

The output of amplifier A (22) is fed to gate Q4 (Figure 13) which solves the Boolean equation $E = F \cdot H \cdot J$. Inputs F and H are high (true), if the pH level is within the normal control range. Input J is high when the pH is at a level to warrant addition of hydrofluoric acid. If the output, E, of gate Q4 is high, relay 7CR will be energized and cause timer 3TR to run for 10 minutes. The timer energizes the concentrated hydrofluoric acid addition pump for the complete 10 minute time period, which is sufficient to raise the bath normality 0.4 unit.

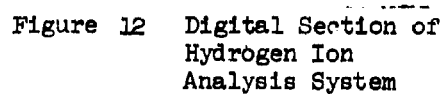
Gate Q5 is used to inhibit the addition system until the proper point in the cycle has been reached and the analog circuit has had a chance to settle. Gates Q10, Q11, and Q12 (Figure 13) are used to generate the system timing pulses) and the time delay for gate Q5. The clock pulses perform several functions. First, they control the current pulses to the "ALARM" lamp which is controlled from any of the emergency stop switches (Figure 10). Second, they provide a pulse to the stepping switch, which commands it to step to the next position. Since the clock pulses cycle at a repetition rate of about one pulse per two seconds and

since the stepping switch must step every 10 seconds, a counter is used to count 30 steps. Clock pulses are fed to gate Q20 which is a decimal counter (Figure 14) that resets after a count of nine. Output voltage at pin V goes from high to low at the nine-to-zero-count transition. Each time this voltage transition occurs, counter Q21 increments by one. When a clock pulse count of 30 has been reached, pins R and N of counter Q21 are both high. This enables gate Q22 to energize relay 8CR which controls stepping of the stepping switch. Counter Q21 is reset and relay 8CR is de-energized two clock pulses later.

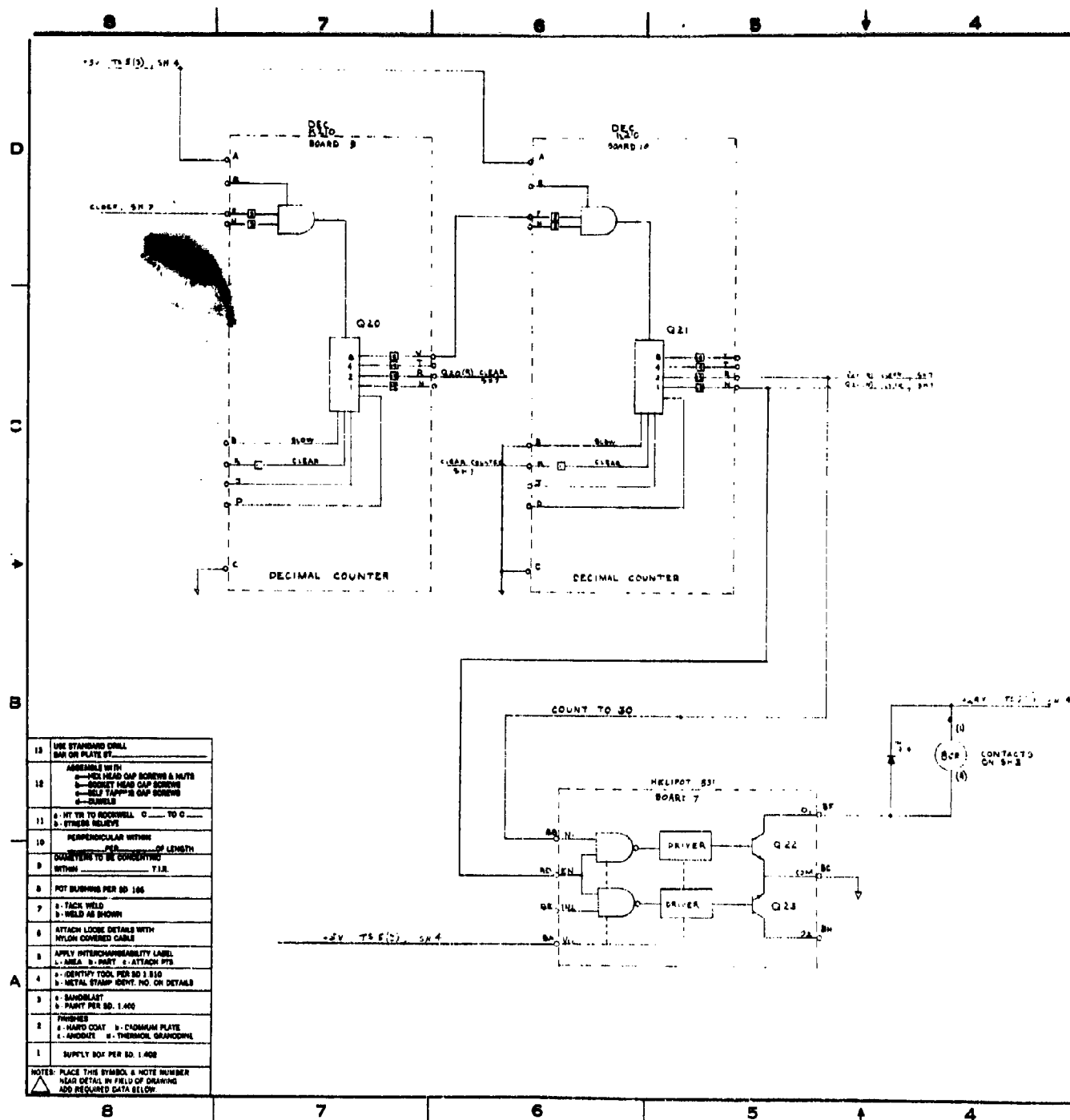
4. AUTOMATIC ANALYSIS OF TITANIUM CONCENTRATION

Automatic analysis of the bath titanium concentration is required to determine when and for what period of time the centrifuge must operate. To simplify the analysis, the titanium concentration should vary only between 10 and 20 grams per liter. A 10-gram-per-liter increase in titanium concentration will be permitted to make full use of the processing capability of the Sharples 30-inch centrifuge. This change can be easily detected by hydrometric and ultrasonic measuring techniques. Tests have shown that the specific gravity of the bath changes about 6.5 percent as titanium concentration increases from zero to 30 grams per liter of titanium.

The ultrasonic technique relates the velocity of a sound pulse through the liquid to the density of the liquid. A transmitting and receiving transducer is submerged at a fixed distance in the solution. A generator produces a sound pulse; the transit time or frequency is then measured. Etchant samples were sent to the Electronic Systems Division of the N.U.S. Corporation in Paramus, New Jersey. Sound velocity measurements were performed on a fresh, 10-percent hydrofluoric acid sample and on one with 20 grams per liter of titanium. Sound velocity at 23°C increased significantly from 1458.4 to 1489.9 meters per second due to the presence of titanium. The temperature coefficient of sound velocity at 23°C correspondingly decreased from 2.19 to 1.67 meters per second per degree Centigrade. These findings indicate that ultrasonic devices can be used to monitor titanium concentration to an accuracy of 0.6 gram per liter provided that temperature is held within 0.5°C or that temperature compensation is used. The N.U.S. Corporation manufactures laboratory and industrial velocimeters with proportional voltage outputs that are capable of controlling centrifuge operations. Chemically compatible probe materials are available.



B



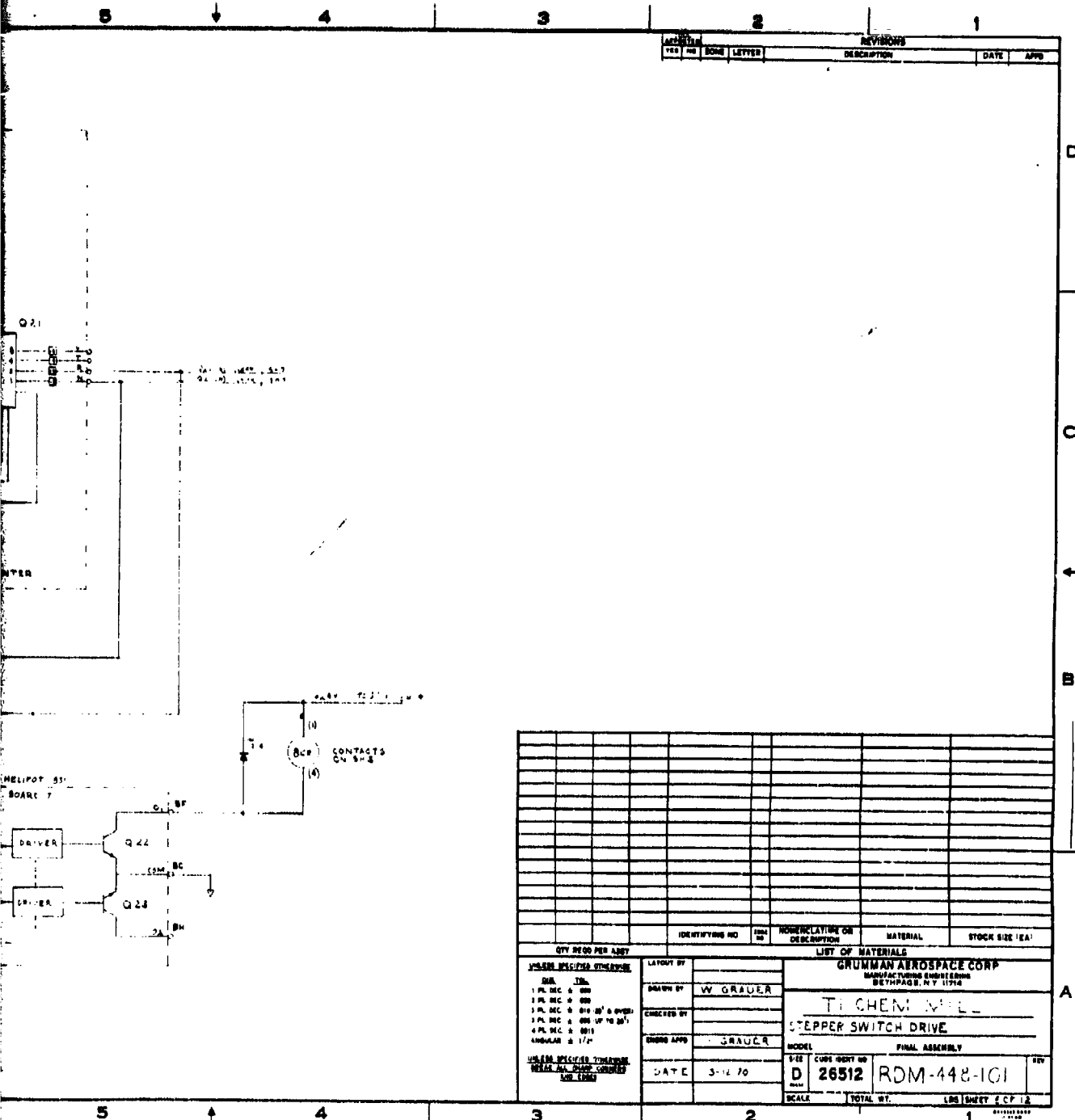


Figure 14 Stepper Switch Drive for Hydro-Fluoric Acid Concentration Control System

Specific gravity can also be determined by the rise and fall of a hydrometer. This method was used to control the reclamation process. The effect of bath titanium concentration on hydrometer rise is shown in Table III. In the automatic specific gravity sensing system that was designed (Figure 15), a hydrometer was modified to intercept a light beam. The position of the hydrometer was determined by illuminating the upper part of the barrel which was painted black. The light source was moved up until light just appeared over the top of the hydrometer barrel. A photocell that moved with the lamp was used as the feedback device. Standard glass hydrometers were given a coating of polyvinyl chloride to fit them for use in hydrofluoric acid solutions. The hydrometers were recalibrated from zero to 25 degrees Baume.

TABLE III
HYDROMETER RISE TESTS

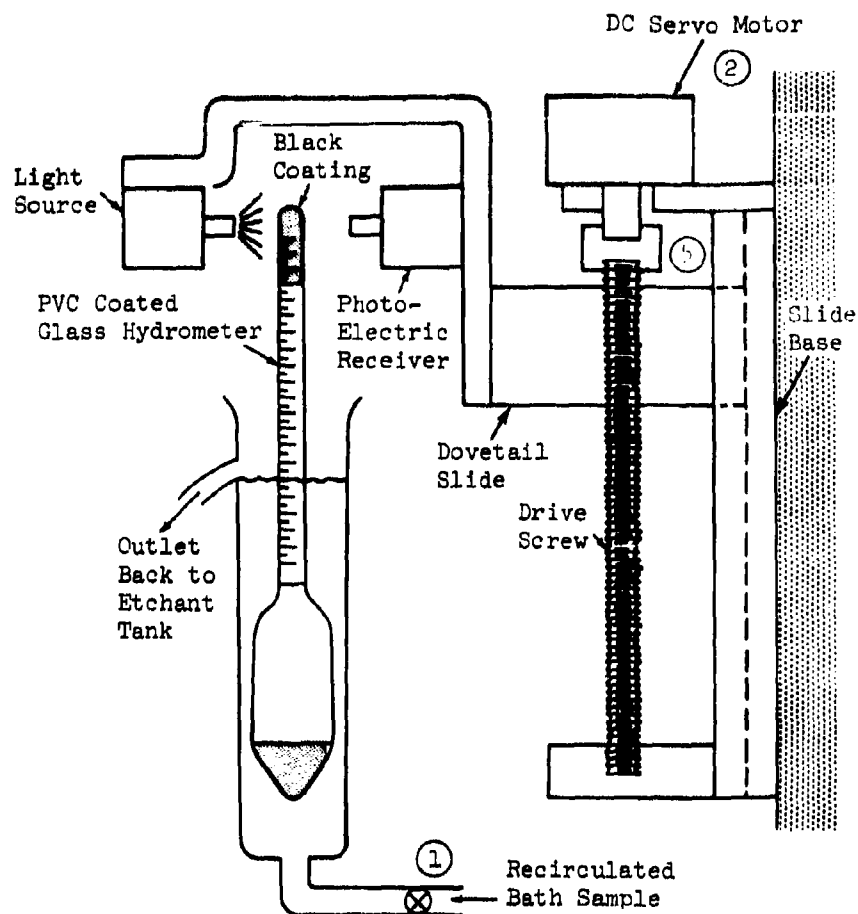
| TITANIUM CONC., GRAMS/LITER | BATH CONC., DEGREES BAUME | DENSITY, GRAMS/MILLILITER | HYDROMETER RISE, INCHES |
|--------------------------------|------------------------------|------------------------------|----------------------------|
| 0 | 3.5 | 1.025 | 0 |
| 10 | 6.5 | 1.047 | 1.375 |
| 20 | 9.5 | 1.070 | 2.750 |
| 30 | 12.5 | 1.094 | 4.125 |

The hydrometer method has a cost advantage over the ultrasonic method. A hydrometer system was built for about \$400. A laboratory ultrasonic system would cost about \$1,000 - \$2,000, while an industrial system would cost about \$2,000 - \$3,000. The hydrometer rise is accurate to within plus or minus 1/16 inch; this corresponds to an analysis variation of less than 0.5 gram per liter. Because of the reclamation process that will be used, the presence of such constituents as tin and vanadium in titanium alloys affects the specific gravity of the etchant slightly. These alloying constituents gradually increase in the tank and only a portion is removed by centrifuging. As a result, the zero point must be changed after each centrifuging. During normal operation the bath is allowed to reach a titanium concentration of 20 grams per liter. If Ti-6Al-4V titanium alloy is being chem-milled, the bath will contain 19.6 grams per liter of titanium and 0.4 gram per liter of vanadium. The centrifuge operates until the bath has been brought down to a concentration of 10 grams per liter. At this point, the bath contains 9.6 grams per liter of titanium and 0.4 gram per liter of vanadium. The addition of another 10 grams per liter of titanium supplies 0.4 gram per liter of vanadium. The hydrometer, therefore, indicates a specific gravity of 20.4 grams per liter even though the bath contains only 19.6 grams per liter of titanium. The centrifuge, then, would operate at a concentration of 20 grams per liter. The next operating point must be at a concentration of 20.8 grams per liter, and so on.

a. Electrical

The hydrometer (Figure 15), whose height measures the amount of titanium in the bath, is interrogated at the same time that the pH meter is interrogated. A potentiometer determines if the hydrometer is above a certain level. If it is, a signal is generated to turn on the centrifuge. The centrifuge cycle was to be timed so that, at the proper feed rates, five grams per liter of titanium would be removed from the bath in one cycle of the centrifuge. More than one cycle was needed, however, to remove five grams per liter from the entire volume. The increase in vanadium amounted to 0.112 gram per liter. The circuitry was then biased up by an amount corresponding to a concentration of 0.112 gram per liter. The centrifuge is again activated when the titanium concentration increases by five grams per liter. The photocell is moved by a dc-servo motor attached to a lead screw. A potentiometer tied to the lead screw monitors the position of the photocell. Each time that five grams per liter of titanium have been removed from the bath, a stepper switch increases the voltage to the comparator-summing amplifier by a fixed amount. The dc-servo motor rotates the lead screw until the photocell goes over the top of the hydrometer. This process is continued until 80 grams per liter of titanium have been removed. At this point the biasing circuitry will be automatically re-zeroed. To comply with this, the hydrometer is then manually re-zeroed based on a laboratory analysis.

Power for the hydrofluoric acid and titanium analyzers is supplied by a solid-state, alternating current regulator (Figure 16). This system supplies true sine wave, constant-rms voltage to the individual power supplies and the pH meter (Figure 17). The output is constant to ± 0.1 percent rms for an input voltage ranging from 105 to 130 volts (ac). In addition, frequency regulation is less than 0.002 percent per cycle and the standby power drain is less than 10 percent of the full-load power input. Response time is less than one period of the input waveform. Output is rated at 500 VA.



| Solenoid Control Valve Switch No. | One-Minute Stepping Intervals | | | | | | | | | | | | | | | | | | | | Operation |
|-----------------------------------|-------------------------------|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | |
| ① | | | | | | | | | | | | | | | | | | | | | Exchamt Solution Circulating; Pump Off |
| ② | | | | | | | | | | | | | | | | | | | | | Activate Drive so Photo-Cell Can Find End of Hydrometer |
| ③ | | | | | | | | | | | | | | | | | | | | | Recount Titanium Level |
| ④ | | | | | | | | | | | | | | | | | | | | | Start Centrifuge Cycle |
| ⑤ | | | | | | | | | | | | | | | | | | | | | Adjust Rack For New Vanadium Level for Next Cycle |

Figure 15 Automatic Hydrometer Specific Gravity Sensing System

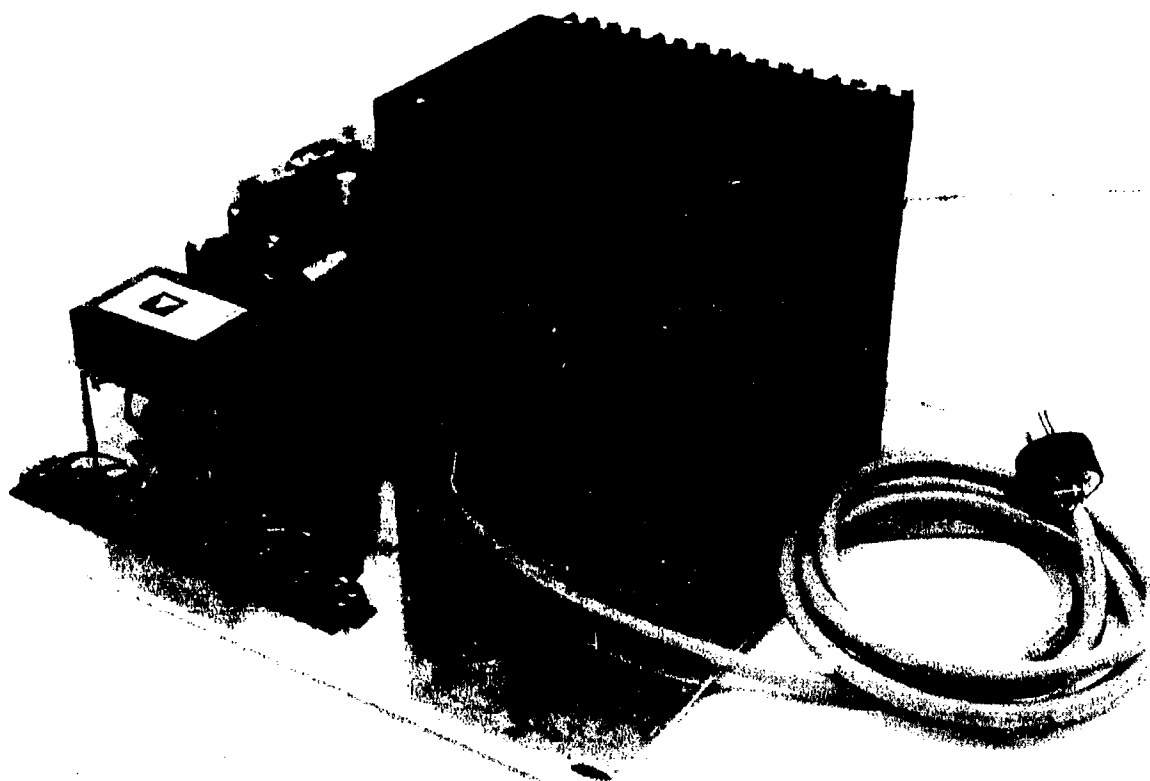
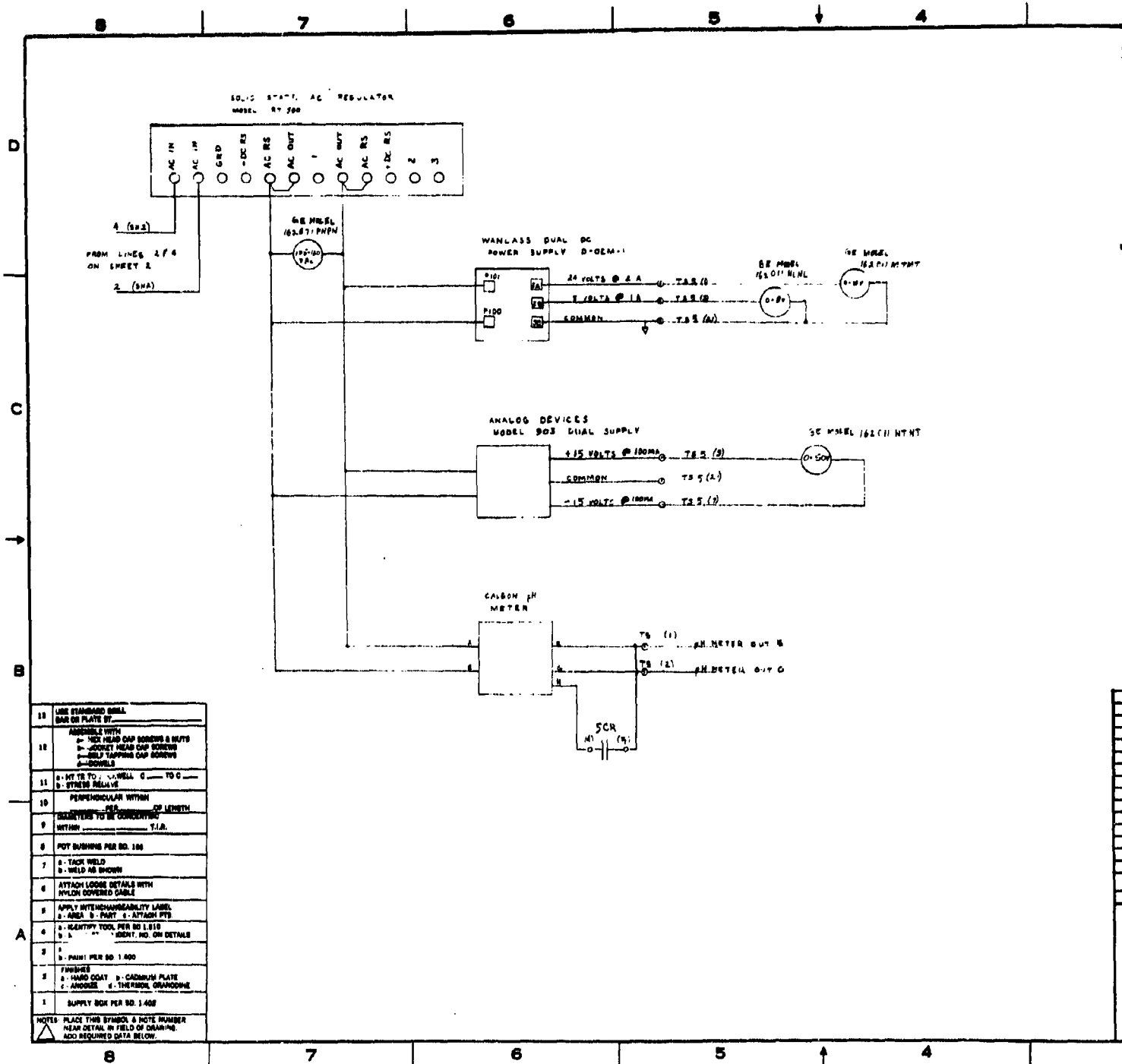


Figure 16 Solid-State Regulator and Power Supply for Hydrofluoric Acid and Titanium Analyzers



| | |
|----|--|
| 13 | USE STANDARD DRILL BAR ON PLATE 07. |
| 12 | ASSEMBLE WITH: a. 1/4" HEX HEAD CAP SCREWS & NUTS b. 1/4" SOCKET HEAD CAP SCREWS c. SELF TAPPING CAP SCREWS d. WASHERS |
| 11 | a. MTS TO 1/4" HELL G TO G b. STRESS RELIEVE |
| 10 | PERPENDICULAR WITHIN |
| 9 | MEASUREMENTS TO BE CONDUCTED WITHIN T.I.R. |
| 8 | POY BUSHING PER SD. 100 |
| 7 | a. TACK WELD b. WELD AS SHOWN |
| 6 | ATTACH LOOSE DETAILS WITH NYLON COVERED CABLE |
| 5 | APPLY INTERCHANGEABILITY LABEL: a. AREA b. PART c. ATTACH PTS |
| 4 | a. IDENTIFY TOOL PER SD. 1.810 b. 1/4" IDENT. NO. ON DETAILS |
| 3 | a. PAINT PER SD. 1.400 |
| 2 | FINISHES: a. HARD COAT b. CADMIUM PLATE c. ANODIZE d. THERMOGRANULINE |
| 1 | SUPPLY BOX PER SD. 1.400 |

NOTES: PLACE THIS SYMBOL & NOTE NUMBER NEAR DETAIL IN FIELD OF DRAWING. ADD REQUIRED DATA BELOW.

Handwritten signature or mark.

The height of the hydrometer for measuring the amount of titanium in solution is determined by moving a photocell/light combination until the top of the hydrometer breaks the light path. The rack bar (Figure 18), which holds the photocell/lamp combination, is moved by a small dc-servo motor. When the light beam is intercepted, Amplifier A (11,1) (Figure 19) is saturated, causing the servo motor to reverse. The motor will then cause the light beam to move above the hydrometer, saturating the amplifier in the other direction. As a result, the light beam will move slightly up and down on top of the hydrometer. This oscillatory motion will not impair the accuracy of the measuring system because the degree of oscillation is designed to be very small. The wiper of a potentiometer mounted to the motor will be calibrated to indicate the height of the hydrometer. The output signal of the potentiometer is fed to Amplifier A (12, 1) where it is compared with the output of the digital-to-analog (D/A) converter. If the output of A (12,1) is greater than the set point titanium concentration, the centrifuge will be activated and stay on for a certain length of time. The time is selected so that five grams per liter of titanium will be removed. The D/A converter is necessary because the system must be automatically readjusted after every centrifuging operation to account for the amount of aluminum and vanadium left in the bath. This is done by changing the bias to Amplifier A (12, 1) in discrete steps. Each time a centrifuging operation is performed, a stepping switch (Figure 20) steps by one position. The stepping switch has four banks and is wired for a four-bit binary output. Four lamps on the front panel are used for indicating how many centrifuging operations have been performed. The readout is in binary form with the lamps representing weights of 1, 2, 4, and 8 respectively. The binary output of the lamps are fed to the D/A converter consisting of Q33, through Q36 and resistors R (13, 1) through R (13, 6). The D/A converter consists basically of four FET's (field effect transistors) used for current switching and the necessary input level shifting circuitry. The output current, which now is proportional to the number of centrifugings, is fed to Amplifier A (12, 1).

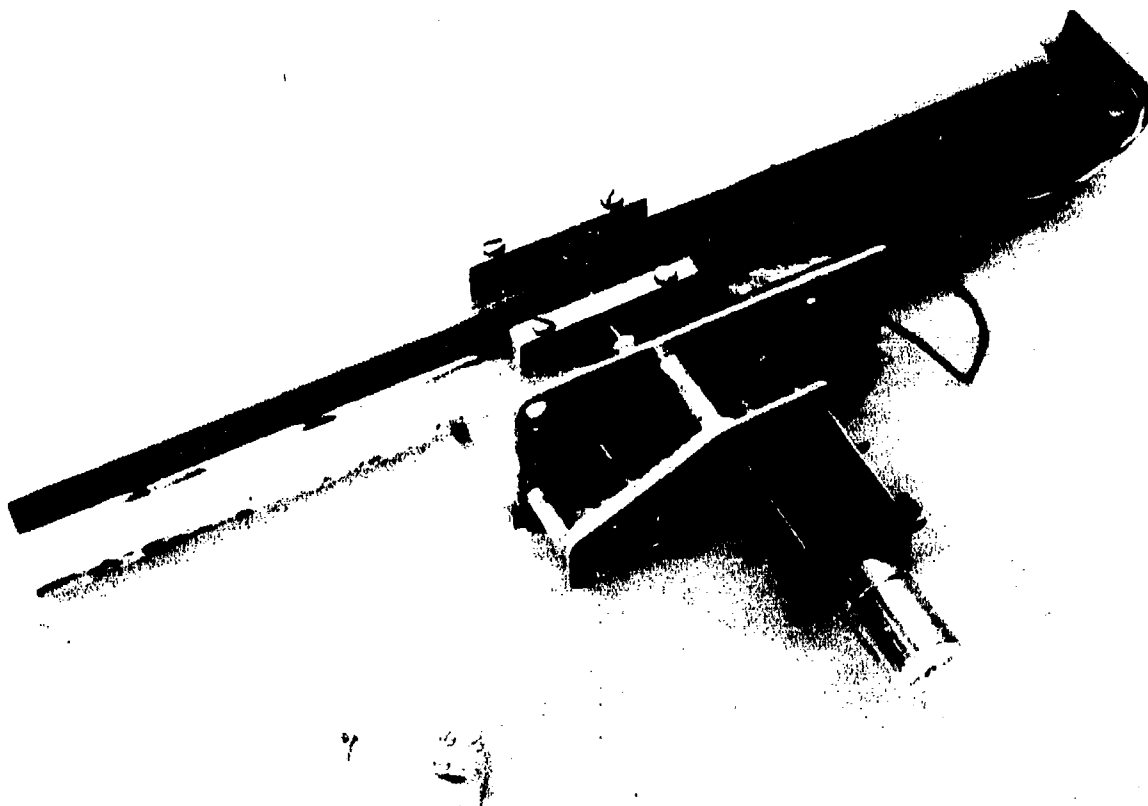
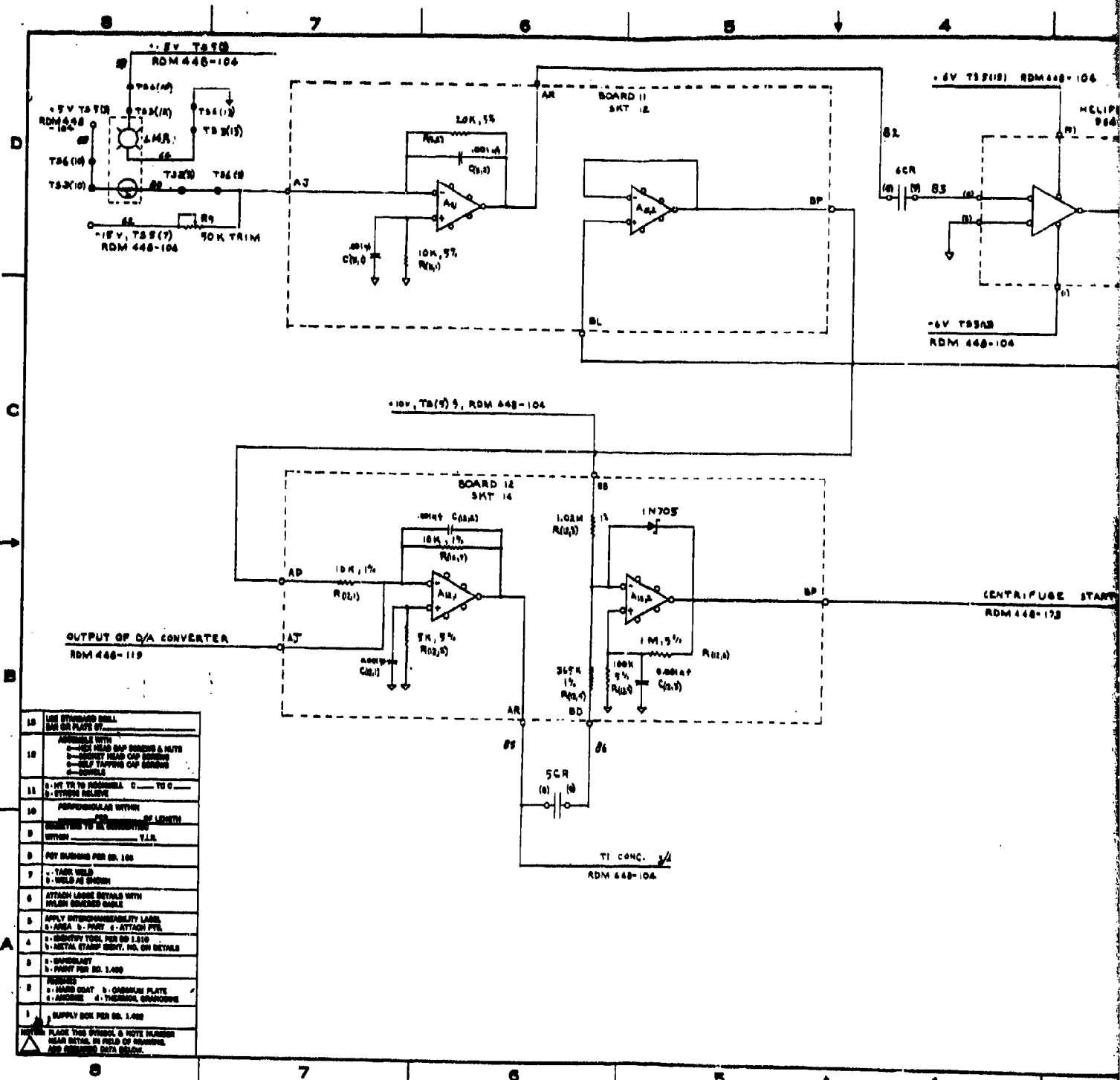
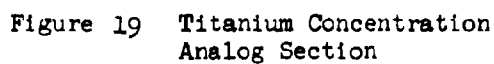
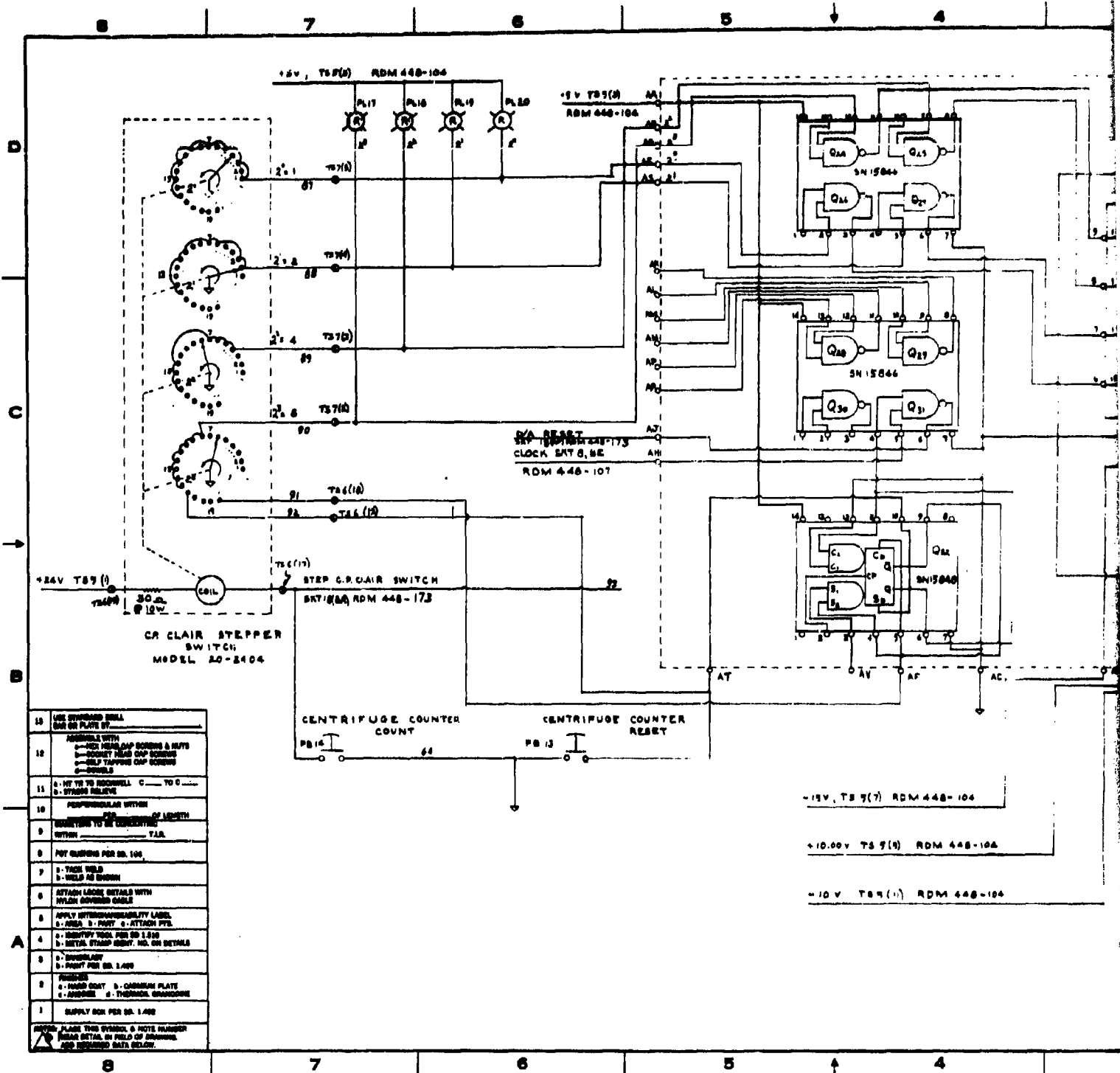


Figure 18 Rack and Pinion for Moving Photocell/Light Unit







| | |
|----|---|
| 10 | USE STANDARD BELL CIRCUIT PLATE OF |
| 12 | ASSEMBLE WITH a. HOLE HEAD CAP BOWING & NUTS b. SOCKET HEAD CAP BOWING c. SELF TAPPING CAP BOWING d. SCREWS |
| 13 | a. HOLE TO BOWING C TO C b. STROKE RELIEF |
| 14 | PERPENDICULAR WITHIN OF LENGTH |
| 15 | BOUNTING TO BE CONCENTRIC WITHIN T.A. |
| 16 | FOR BOWING PER SO. 104 |
| 17 | a. TACK WELD b. WELD AS SHOWN |
| 18 | ATTACH LOCK DETAILS WITH TWIGG COVERED GABLE |
| 19 | APPLY IDENTIFICATION LABEL a. AREA b. POINT c. ATTACH PPS |
| 20 | a. IDENTIFY TOOL PER SO. 1499 b. METAL STAMP IDENT. NO. ON DETAILS |
| 21 | a. OVERLAY b. POINT PER SO. 1499 |
| 22 | FINISH |
| 23 | a. HARD COAT b. CARBIDE PLATE c. ANODIZE d. THERMAL BRONZING |
| 24 | SUPPLY BOX PER SO. 1499 |
| 25 | NOTE: PLACE THIS SYMBOL & NOTE NUMBER BEHIND DETAIL IN FIELD OF DRAWING AND INCLUDE DATA BELOW |

41/42

When the concentration of titanium is high enough to call for a centrifuging cycle, the controller sequentially starts the centrifuge pump and the centrifuge cycle circuit through relay contacts 9CR and 10CR (Figure 21). The relay coils are energized by logic circuitry driven by the output of A (12, 2) (Figure 19). The coils are not operated at the same time, in order to allow the pump to come up to speed before beginning to rotate the drum.

a. Mechanical

Sampling bath etchant is fed into the bottom of the polyvinyl chloride (PVC) hydrometer overflow cylinder and exits through the side overflow aperture. A hole in the center of cover centers the hydrometer stem. A larger hole in the baffle guides and centers the hydrometer barrel. The center baffle and cylinder bottom are fusion welded to the hydrometer barrel. Holes in the baffle allow etchant to circulate up and through the overflow cylinder with a minimum of turbulence. The cover can be removed to provide room to replace the hydrometer.

The flow of etchant solution through the automatic analyzer begins at a previously determined, timed interval before analysis takes place so that a representative sample will be drawn. The etchant solution is pumped from the etchant tank to the analyzer by a Model 9101-11 Precision chemical pump (Figure 22) at a controlled speed. Since the system is open because of flow into the vented top hydrometer cylinder, another pump of the same type must be used to return the etchant solution to the etchant tank. As a precaution against failure of the return pump to operate during the sampling cycle, the hydrometer cylinder overflow feeds into a polyvinyl chloride (PVC), cylindrical sump tank that has sufficient capacity to hold the entire quantity of sampled etchant solution.

5. AUTOMATIC REMOVAL OF TITANIUM FROM ETCHANT SOLUTION AND RECLAMATION OF HYDROFLUORIC ACID

a. Centrifugal Etchant Reclamation System

When the analyzer indicates that the hydrofluoric acid in the etchant solution needs replenishing, a Model 1190 Randolph pump (Figure 23) is started automatically and timed to move the correct amount of acid from the holding tank to the etching tank.

This is accomplished by a "squeegee" action on a continuous flexible PVC tube that connects both tanks. This pumping system permits visual inspection and eliminates corrosion problems, since the hydrofluoric acid never contacts any part of the pump but only the PVC tube passing through the pump.

Potassium fluoride is added to the etchant bath to obtain a potassium fluotitanate precipitate that can be removed with a centrifuge. Experience has shown that forming of the precipitate in the chem-mill tank should be avoided. Potassium fluoride is introduced, therefore, into the centrifuge input line rather than the tank itself. After the upper titanium concentration limit (about 20 grams per liter) has been reached, the titanium analyzer provides the signal to start the centrifuge, the hydrofluoric acid pump to the centrifuge, and the potassium fluoride on-line mixer. These components continue to operate until one centrifuge cycle is completed. No attempt is made to remove all of the titanium from the solution because of the possibility of recirculating potassium fluotitanate back to the etchant tank and causing a gradual buildup of precipitant on the bottom of the tank.

The centrifugal reclamation piping system shown in Figure 24 operates as follows: A signal from the titanium analyzer to start the reclamation cycle indicates that the centrifuge should be turned on. When the hydrometer photocell signals for titanium removal, a latching type of relay is activated. This starts the centrifuge oil-gear-pump and, a short time later, starts the centrifuging cycle. After the centrifuge basket reaches a speed of 1,450 revolutions per minute, pumps 2 and 3 draw fluid from the spent hydrofluoric acid and potassium fluoride tanks. In-line mixing of these constituents takes place in pump 2 where sufficient turbulence causes complete precipitation. The output of pump 2 is then adjusted to obtain the correct proportion of saturated potassium fluoride to precipitate 20 to 25 percent of the titanium concentration. When the sludge on the walls of the centrifuge builds up to a preset thickness, pumps 2 and 3 are turned off. The skim tube is advanced to remove from the sludge the surface liquid acid which is sent back to the etchant tank. The skin tube is then retracted and the centrifuge is decelerated to a speed of 80 rpm. The plow blade moves inward, scraping the sludge off the walls and depositing it in the drum below the unit.

Calibrated, metered pumping systems have been installed to maintain the desired ratio of potassium fluoride in the etchant solution when both the etchant and potassium fluoride solutions are being pumped into the centrifuge for precipitation and removal of titanium. The potassium fluoride solution is pumped by a Model

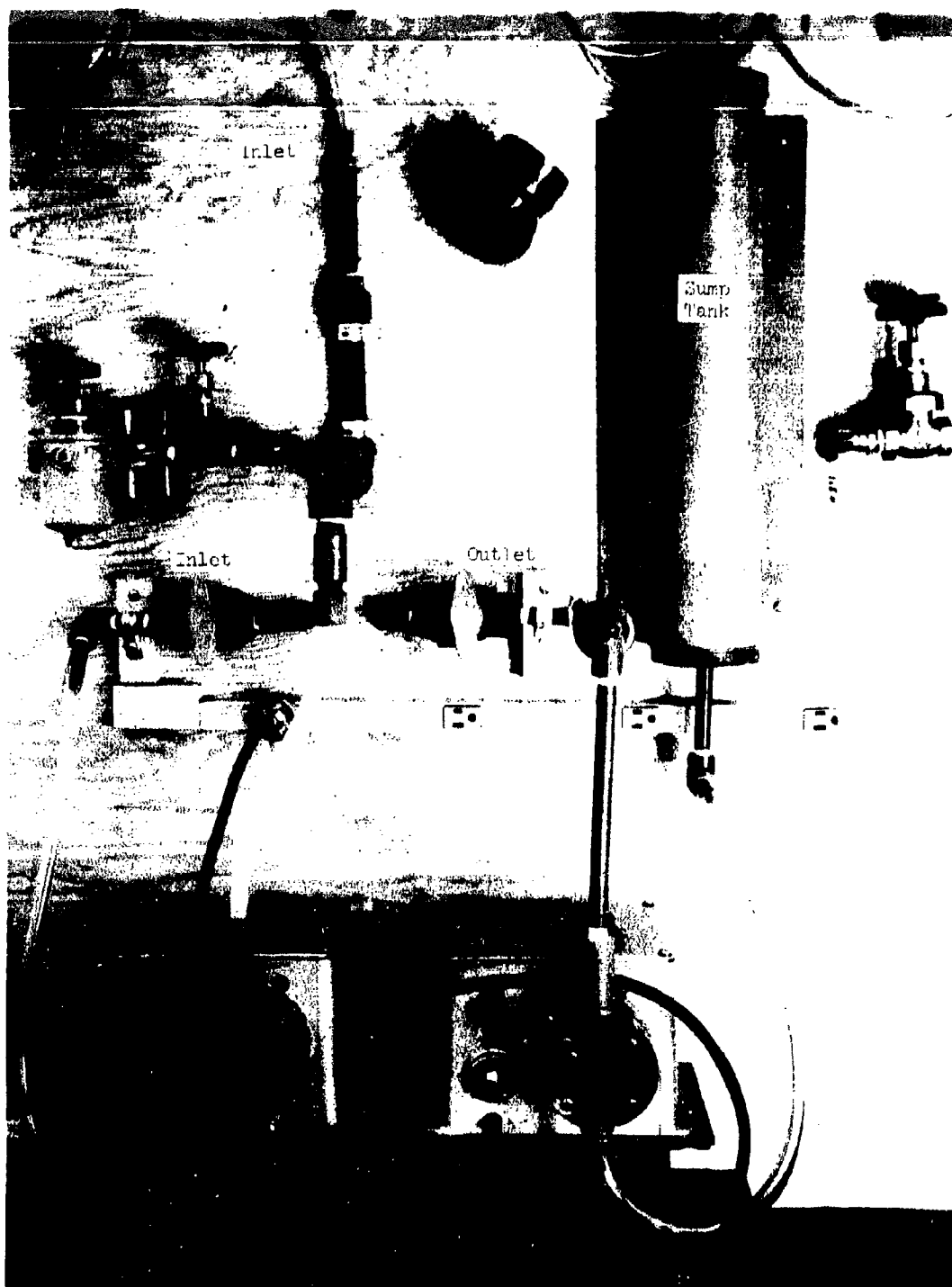
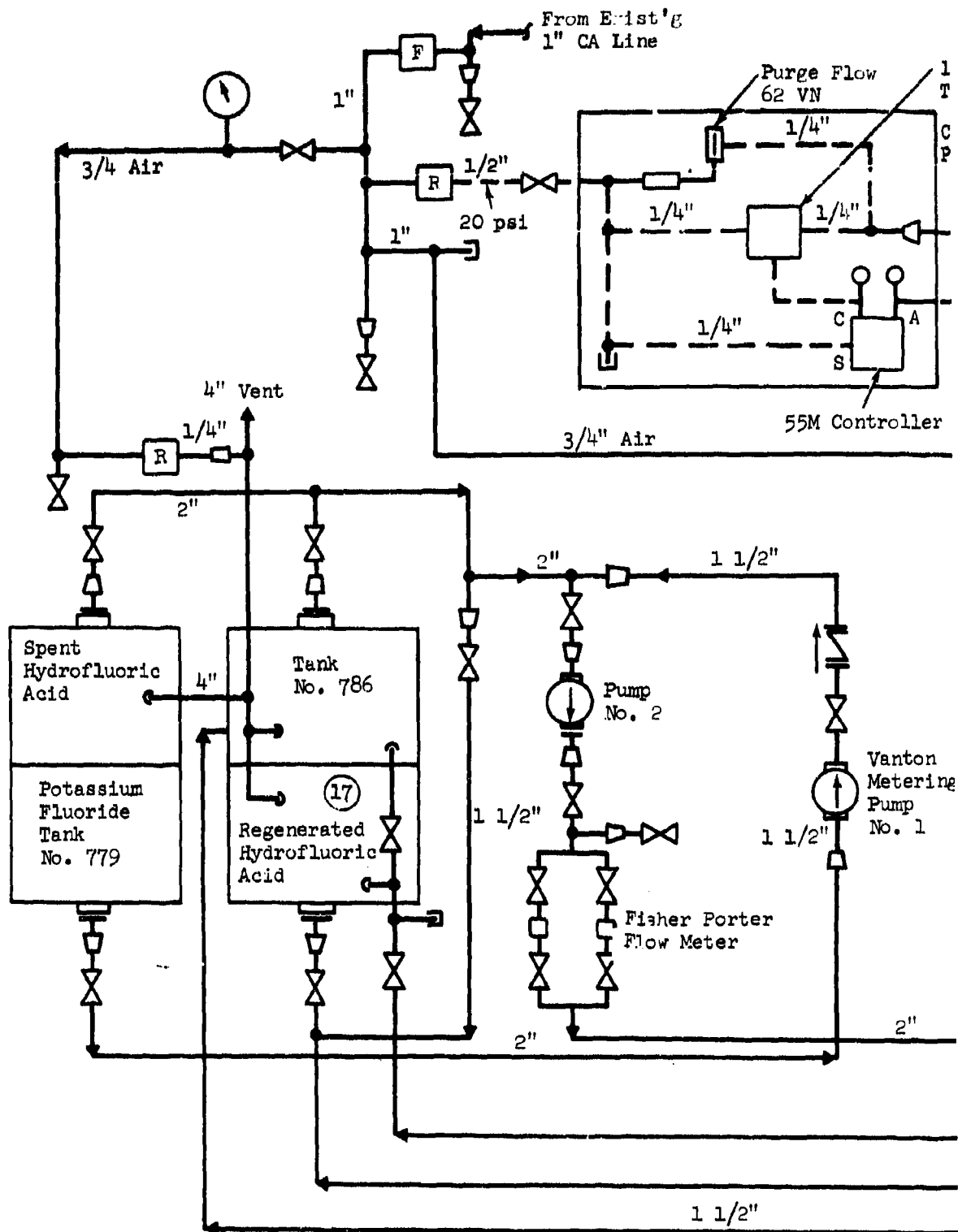


Figure 22 Precision Chemical Pumps



Figure 23 Centrifugal Regeneration Tanks and Control Room



174 P
Transmitter

Control
Panel

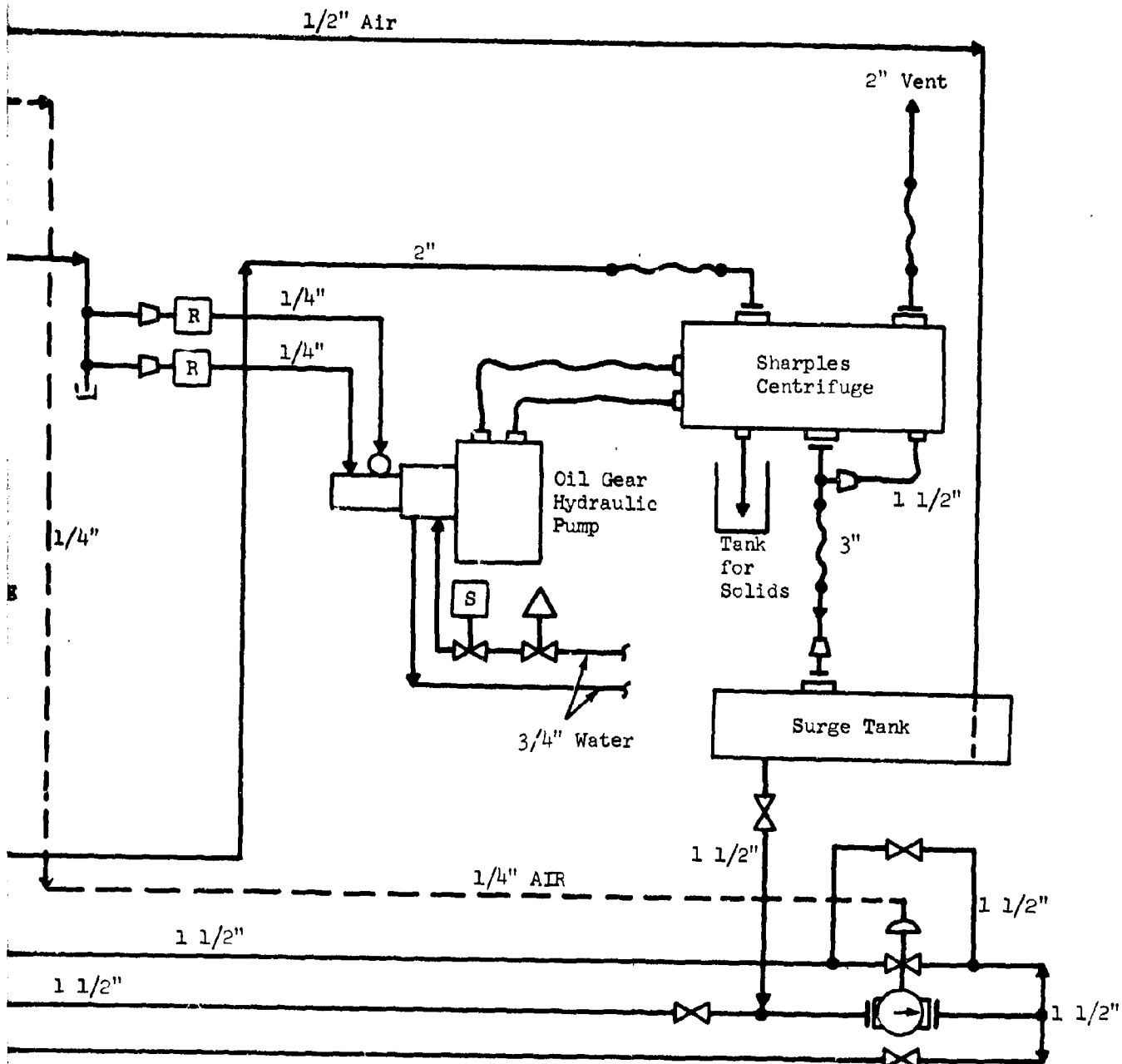


Figure 24 Centrifugal Reclamation
Piping Diagram

49/50

B

60-A Vanton seal-less plastic pump powered by a 1/2-horsepower 1,725-rpm, single-phase motor (Figure 25). Flow is adjusted by a throttling valve and measured by a calibrated pressure gage. The etchant solution is pumped from the etching tank to the centrifuge by a pump made by the Industrial Filter and Pump Company. This pump is powered by a two-horsepower, 1,725-rpm, single-phase motor. Flow in this system will be set at a rate of 15 gallons per minute and monitored by a flowmeter. The complete centrifuge system is shown in Figures 26, 27, and 28.

b. Testing of the Centrifugal Reclamation System

The spent, titanium-saturated, hydrofluoric acid etchant had a titanium concentration of about 25 grams per liter when it was transferred from the chem-milling tanks to the holding tank. Successive centrifuging reduced the titanium concentration to less than one gram per liter. The titanium concentration of the etchant was then raised to 24 grams per liter by dissolving additional titanium metal in the etchant. This process was repeated. Results of the last two cycles are shown in Figure 29. Reduction of the titanium concentration from 23.8 to 18.2 grams per liter was not counted as a run, because it was a demonstration run during which no data were recorded. The solid line in Figure 29 shows the accumulated loading of the bath if no titanium had been removed; the long-dash line shows the drop in titanium concentration as each centrifuge run was completed. These data were obtained by atomic flame emission analysis of the etchant at the conclusion of each run. Although this analytical technique is probably only accurate to within only one gram per liter, the overall slope of the line generated from successive runs is felt to be representative of the unit's capability.

Since the 450 gallons of etchant that were treated during each run through the centrifuge were returned to the same tank from which it was drawn, the entire 957 gallons of etchant can be considered to have been treated. The total amount of titanium removed from the etchant tank was less than that removed from the acid run through the centrifuge by the ratio of the volume run through the centrifuge to the total amount in the tank.

The amount of potassium fluoride used was determined by measuring the height of the liquid in the potassium fluoride tank before and after each run and multiplying the volume used by the specific gravity of the liquid. The following stoichiometric equations were used together with the total volumes of potassium fluoride solution and etchant to calculate the theoretical amount of titanium that can be removed in each run:

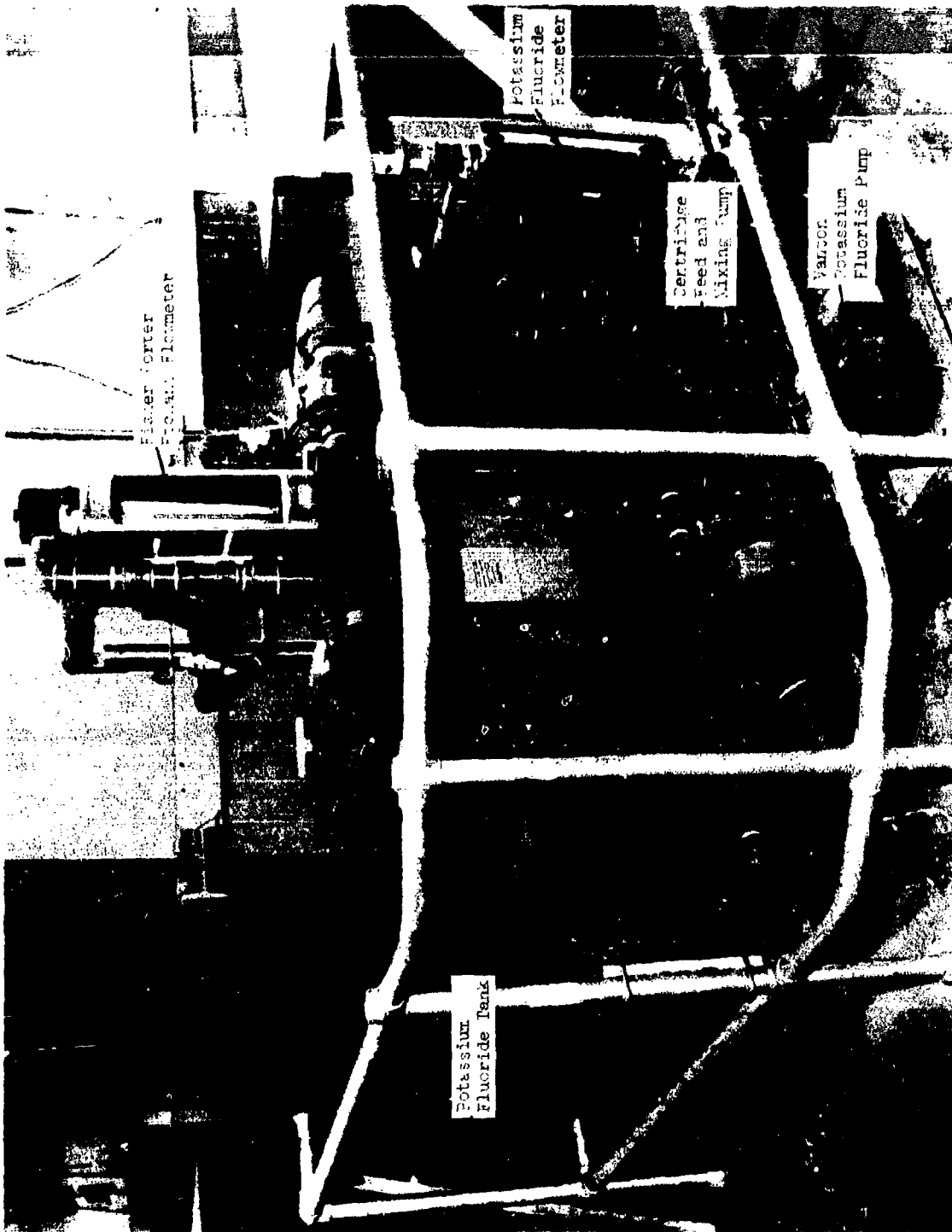


Figure 25 Centrifugal Precipitation and Feed Pumps



Figure 26 Sludge Collection System

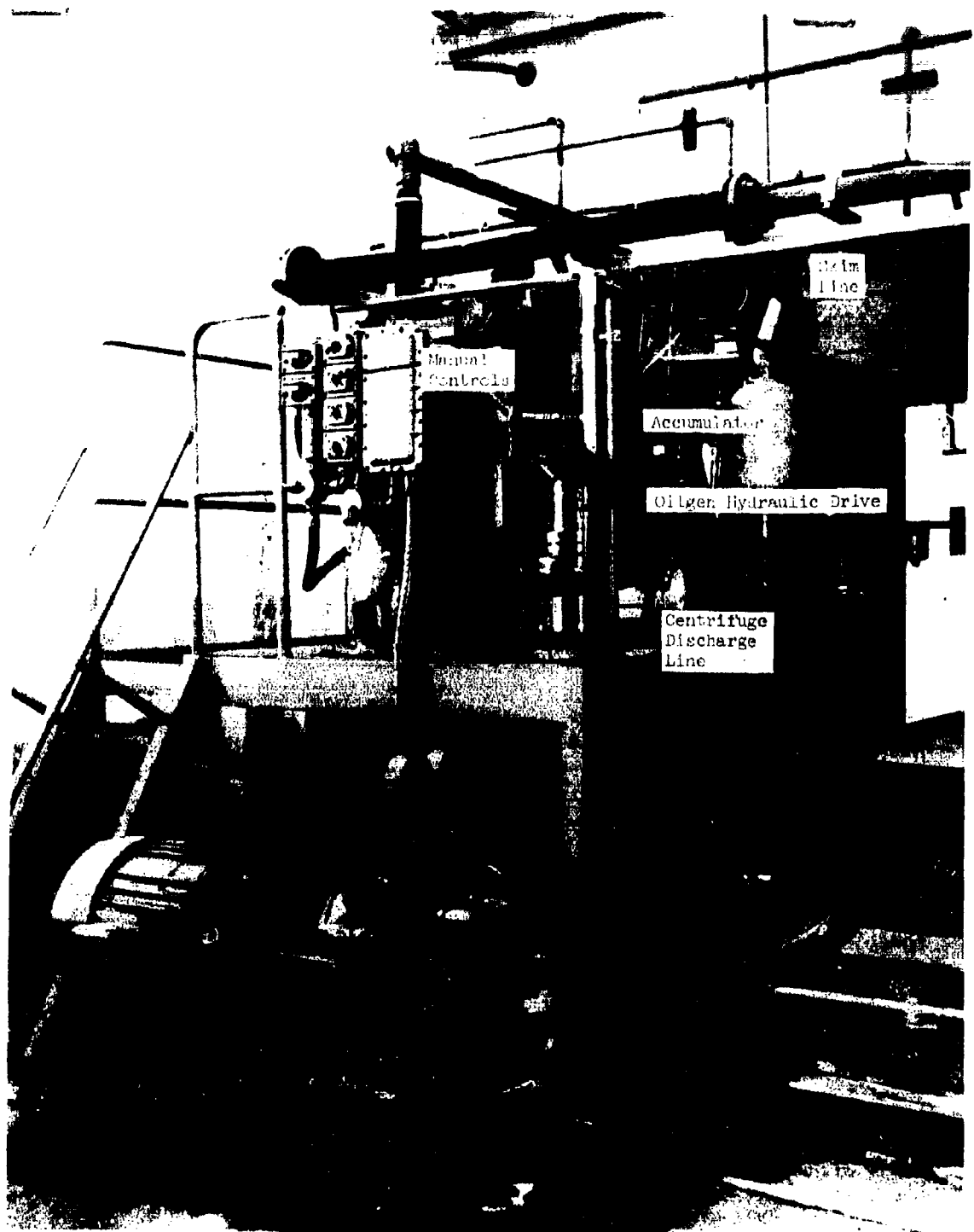


Figure 27 Hydraulic Drive System and Other Mechanical Components of the Centrifuge

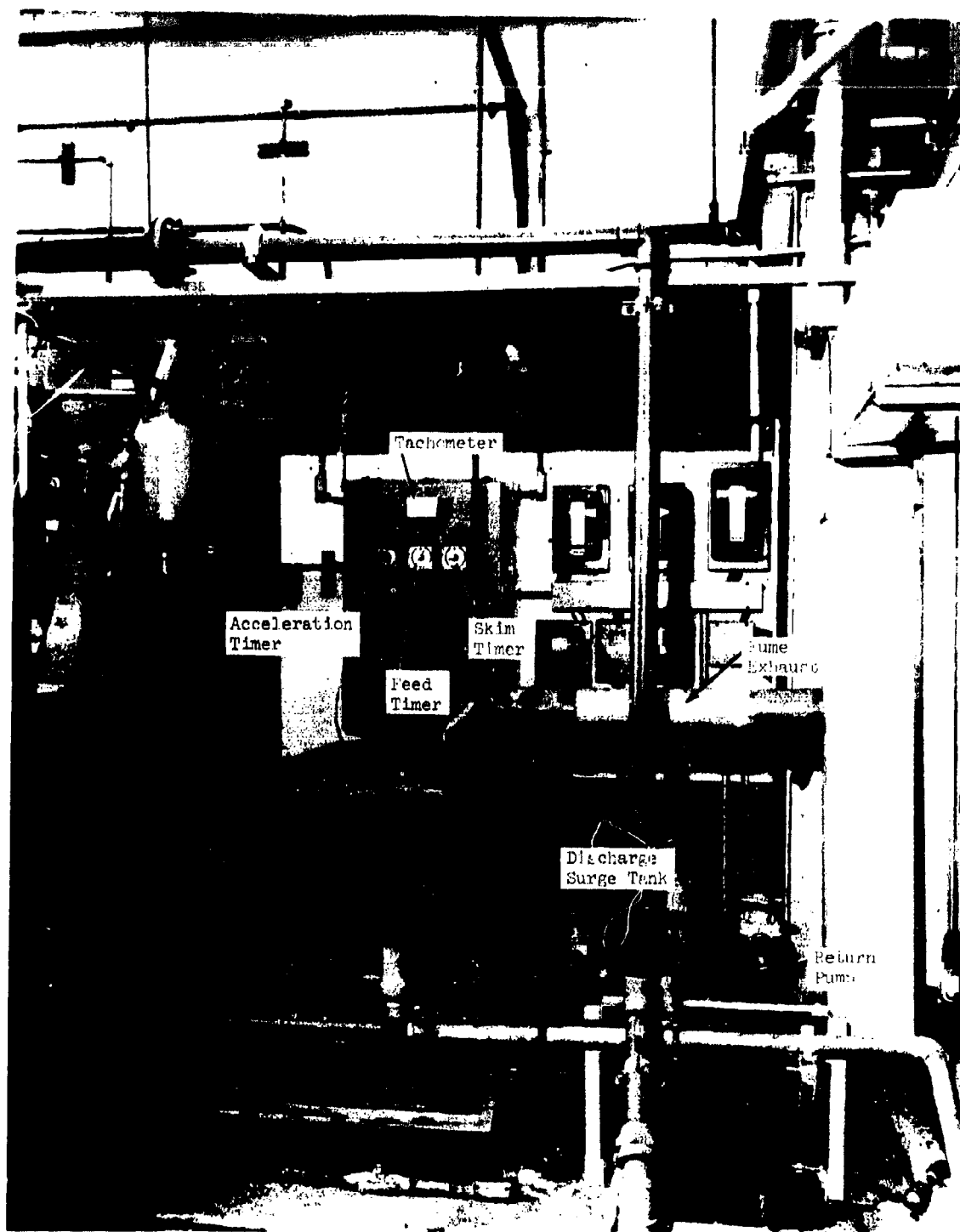


Figure 28 Timing and Discharge Systems for the Centrifuge

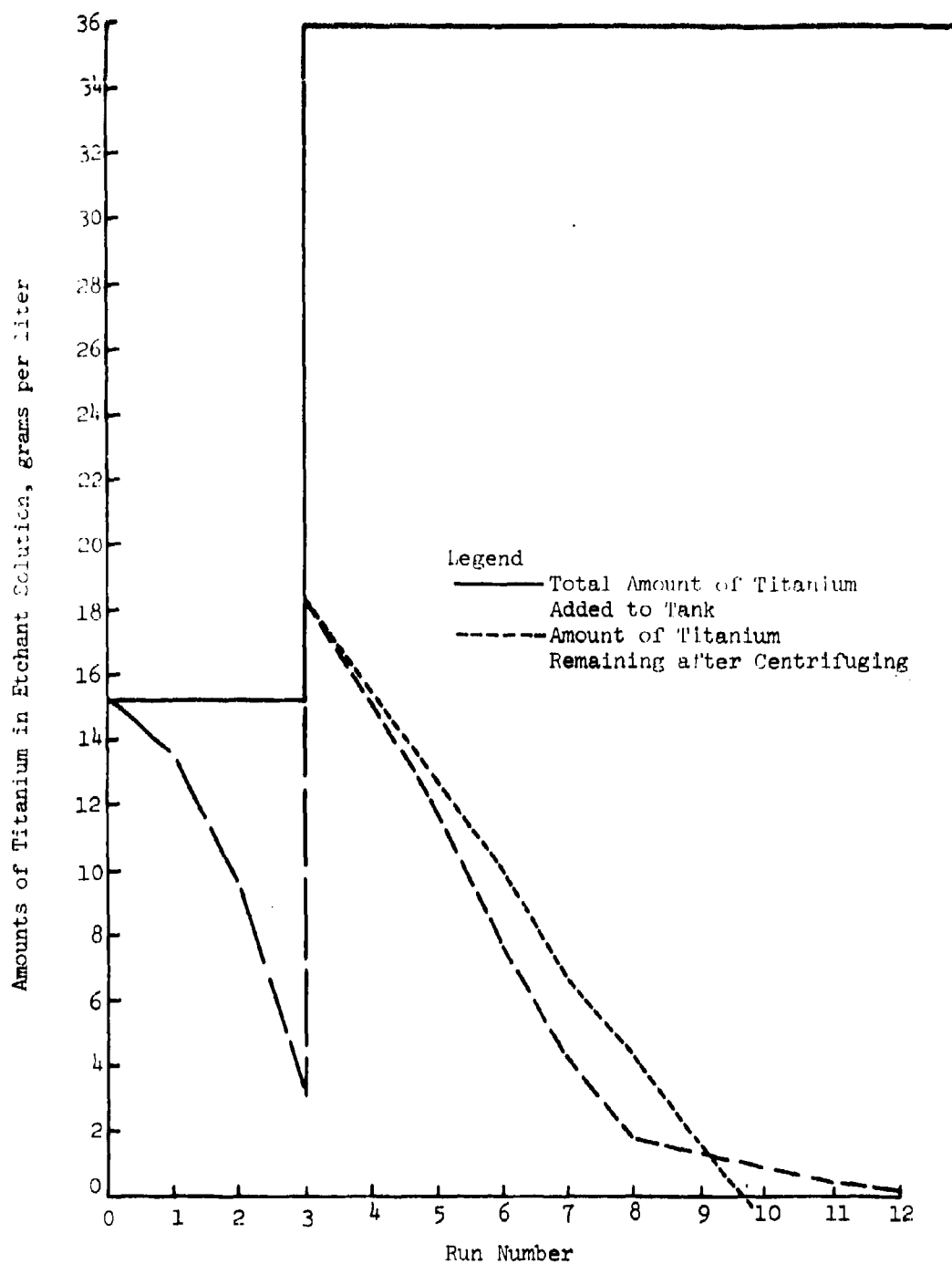
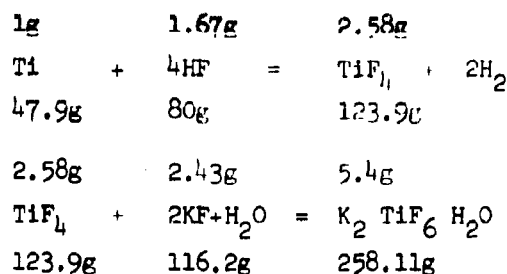


Figure 29 Effect of Centrifuging on Titanium Concentration in Hydrofluoric Acid Etchant



The theoretical and actual amounts of titanium removed are shown in Figure 30. The theoretical amount of titanium that can be removed is less than the actual amount removed, because the vanadium and aluminum alloying constituents are also removed by the potassium fluoride.

Immediately after titanium metal was dissolved in the hydrofluoric and etchant, a brown precipitate appeared in the etchant that was removed by centrifuging even though potassium fluoride was not added. The precipitate was subjected to X-ray diffraction and optical emission spectrographic analyses and was found to consist primarily of aluminum and vanadium compounds. The potassium fluoride that was found to be present in the etchant was the result of previous runs in which an insufficient amount of titanium was available to react with all of the potassium fluoride present. This situation accounted for the precipitation of potassium fluotitanate during centrifuging and the removal of more titanium from the etchant than was theoretically possible. Part of the potassium fluoride needed is already in solution and the remainder of the unaccounted for precipitate is in the form of titanium and vanadium salts. This was borne out in runs 11 and 12 (Figure 29) in which the titanium content was less than one gram per liter and in which a considerable quantity of sludge was precipitated. Analysis of this bright green sludge -- (the potassium fluotitanate precipitate is white) -- showed that it contained no potassium but consisted entirely of titanium and vanadium salts. It can be concluded, therefore, that the precipitation reaction is very complex. In those cases where the amount of titanium removed is in the range of 10 to 20 grams per liter, however, most of the precipitate will consist of potassium fluotitanate.

Centrifuging the etchant solution progressively each time the bath reaches a titanium concentration over 20 grams per liter will maintain a more than adequate chem-milling capability. The sludge removed in this concentration range consists of white, potassium fluotitanate precipitate which can be used commercially as a grain refiner in the alloying of aluminum.

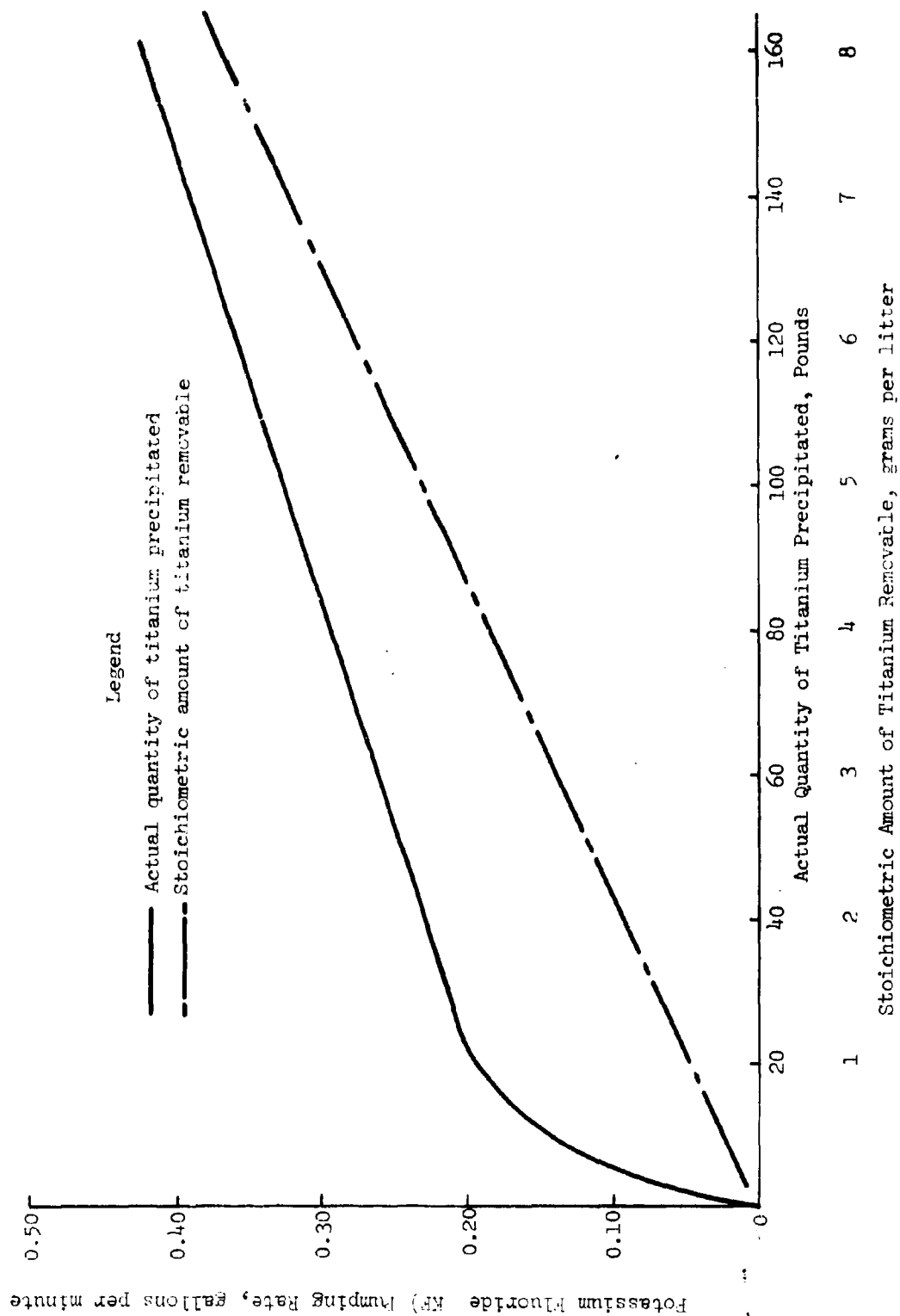


Figure 30 Comparison of Stoichiometric and Actual Amounts of Titanium Removed by Centrifuging

c. Calibration of the Hydrogen Ion and Titanium Concentration Measuring Systems

Automatic titrations were performed to check the accuracy of the hydrogen in measuring system. The pH of the titrated sample was recorded from the display on the system pH meter. The sample was preserved in a container for a subsequent pH determination on a laboratory pH meter. Results of these tests are summarized in Tables IV and V.

TABLE IV
CALIBRATION OF SYSTEM pH METER

| BUFFER SOLUTION pH | READING ON SYSTEM pH METER AFTER CALIBRATION |
|--------------------|--|
| 4.00 | 3.95 |
| 7.00 | 6.90 |
| 10.00 | 10.10 |

TABLE V
COMPARISON OF pH VALUES OF TITRATION SAMPLE

| SYSTEM METER pH | LABORATORY METER pH |
|-----------------|---------------------|
| 12.40 | 11.6 |
| 12.05 | 11.6 |
| 12.20 | 11.6 |
| 11.92 | 12.3 |
| 11.25 | 11.7 |
| 12.20 | 11.8 |
| 11.90 | 11.6 |
| 11.72 | 11.2 |
| 12.30 | 11.8 |
| 11.30 | 10.9 |
| 12.10 | 11.6 |
| 11.70 | 11.5 |

It was observed that the pH reading changed with time in an unpredictable manner but by no more than plus or minus 0.2 unit. The time interval involved was about five to ten minutes which was the time delay between pH readings on the system meter and the laboratory meter.

The titanium measuring system was checked by first determining how long it would take to change the solution in the burette by the normal system pumping action. After the burette was filled with 6.6-degree-Baume hydrofluoric acid, 4.9-degree-Baume hydrofluoric acid was pumped in. The overflowing hydrofluoric acid was not allowed to recirculate. The hydrometer gave readings of 6.9 degrees Baume at the start of pumping and 4.9 degrees Baume one hour later. Since an analysis cycle would normally be initiated every 45 to 90 minutes, the time required for complete recirculation change of the solution in the sample tank was felt to be comparable to that selected for the complete analysis cycle.

The titanium measuring system was calibrated by filling the titanium measuring burette with 6.5-degree-Baume, aqueous sodium chloride solution and having the titanium concentration meter read 10.0 grams per liter when the light was at the top of the hydrometer. An 8.0-degree-Baume, aqueous sodium chloride solution was used to calibrate the meter for a titanium concentration of 15.0 grams per liter. The solution concentrations used were close to those specified in Table III.

d. Requirements for Production Implementation

As a result of tests conducted on the centrifuge system, the following recommendations are made to insure trouble-free production implementation:

(1) Centrifuge

- 30-inch-diameter, stainless steel basket with polyvinylidene coating and 1-1/4-inch-diameter holes in horizontal baffles after coating to insure as dry a sludge as possible.
- Centrifuge feed nozzle should be easily removable for cleaning.
- Flow setup on timer to insure complete cleaning of basket
- Pipe from acid pump to centrifuge should be made from clear PVC, be of minimum length, and have a minimum number of fittings (recommended size is 3/4-inch-diameter) to prevent sludge from settling out in pipes

- Precipitate-thickness-sensor foot on skimmer to prevent sludge from being skimmed over into surge tank.
- Centrifuging cycle should be restarted automatically at the completion of each run until five grams per liter of titanium have been removed from the entire content of the tank (about 14 cycles) for a 6000-gallon etch facility.

(2) Solution Handling Equipment

- Acid Pumps - 20-gallon-per-minute, polyvinylidene fluoride-coated, dual system that can be easily removed for cleaning and is equipped for water flushing to reduce sludge build-up on impeller which causes pump binding.
- Surge Tanks - two 600-gallon, two-stage, settling type, PVC-lined to prevent any precipitated sludge from being returned to etch tank.
- Potassium Fluoride Pump - one-gallon-per-minute metering type with vari-speed drive and Teflon body and impeller to provide accurate potassium fluoride flow.
- Flow Meters - magnetic type, polyvinylidene coated.
- Sludge Collector - batch weighing, liquid separating, automatic loading into plastic-coated, 55-gallon drums to eliminate any manual sludge handling.

(3) Mechanical Analysis Equipment

- Sampling burettes should be made from clear PVC and doubled in capacity to enable visual monitoring of correct operation
- All filling and emptying valves should be made from Teflon and individually operated by electric solenoids.
- The maskant and sodium hydroxide solutions should be constantly circulating through the burettes except during measurement. Overflow material should be pumped back to the supply tanks.

(4) Electrical Analysis Equipment

- Automatic recycling control should be added
- Automatic alarm system to signal pump stoppage, excessive line pressure, or ventilation failure should be added.

- Digital print-out recorder with time and date should be used to replace readout dials of pH and titanium levels.
 - Buttons to manually control each solenoid valve separately should be added to facilitate calibration and adjustment.
 - Adequate ventilation should be provided over the burettes and hydrometer tank to prevent acid fumes from corroding the electrical equipment.
 - The titanium analyzer rack should be longer and have a vernier adjustment for calibration.
- e. Comparison of Vendor Techniques and the Grumman-Developed Automated Centrifugal Regeneration Process for Disposal of Spent, Fluoride-Containing, Chemical Milling Solutions

Existing regulations governing the disposal of fluoride-containing waste solutions into the ground, rivers, or at sea are making it necessary to develop effective and economical processes to regenerate chem-milling solutions. This is a particularly serious problem for chem-milling contractors operating in or near large cities. Existing New York State regulations, for example, limit the amount of free or soluble fluorides that can be discharged into the ground to a maximum of one part per million. The fluoride concentration in industrial chem-milling solutions is normally about 125,000 parts per million. The advantages, disadvantages, and typical costs for disposal of fluoride-containing, waste, chem-milling solutions by vendor techniques and by the Grumman-developed, automated, centrifugal regeneration process are summarized in Table VI. Use of the automated, regeneration process would reduce waste solution disposal costs by 50 to 65 percent below that for vendor removal costs.

TABLE VI
COMPARISON OF DISPOSAL TECHNIQUES FOR WASTE,
FLUORIDE-CONTAINING CHEM-MILLING SOLUTIONS

| | VENDOR REMOVAL | AUTOMATED CENTRIFUGAL REGENERATION |
|----------------|--|---|
| Steps Involved | <ol style="list-style-type: none">1. Obtain approved waste disposal vendor2. Pump acid from tank to vendor's truck or barrels | <ol style="list-style-type: none">1. Make up saturated KF solution2. Automatically analyzes HF and titanium concentrations and removes titanium as potassium fluotitanate sludge |
| Disadvantages | <ol style="list-style-type: none">1. Difficulty in scheduling pickup results in production downtime and disposal of solutions not fully spent.2. Vendors sometimes use questionable treatment and disposal methods. Firms supplying waste solutions can be held responsible for vendor pollution damage.3. Fluoride pollution problems are in many cases only transferred from one location to another.4. Safety problems involved in handling toxic and corrosive hydrofluoric acid. | <ol style="list-style-type: none">1. Equipment requirements |

TABLE VI (Continued)

| | VENDOR REMOVAL | AUTOMATED CENTRIFUGAL REGENERATION |
|---|---|--|
| Advantages | 1. No equipment requirements | 1. Process is completely automated. 2. 50% of HF acid is saved. 3. Sludge produced is of a saleable nature as an aluminum gain refiner. 4. Optimum process parameters are maintained, tolerances are improved, time for part checking and production downtime are decreased. 5. Handling of highly corrosive materials is reduced. |
| Estimated Costs for ten, 6,000-gallon loads | 1. \$9,000-\$20,000 depending on vendor 2. \$10,760 for HF acid for tank make-up (\$1.80/gallon) 3. Cost of lost production time. Total Cost - \$19,760 - \$30,760 | 1. Potassium fluoride for additions at \$0.40/lb (\$14,616) 2. HF acid for tank makeup at \$1.80/gallon (\$5,380) 3. \$9,720 returned for sale of sludge at \$0.12/lb. Total Cost - \$10,276 |

SECTION II

MASKANT DEVELOPMENT TASK

1. APPROACH

The masking operation presents cost and technical chem-milling problems such as:

- Pinholes, maskant blowouts during etching; degradation and breakdown in highly concentrated acid solutions
- Floor space requirements and time-consuming sequences; usually two or three maskant coats are required with drying time between; parts must be rotated during coating; oven curing may be required
- Overall cost and man-hour efforts for repair, inspection, and scribing
- High degree of dependence on operator scribing skill

The conclusions reached as a result of this study are:

- An improved, low-cost, styrene-butadiene maskant was developed that meets all chem-mill maskant requirements, including smoothness and uniformity of coating surface, good scribing and peeling characteristics, and resistance to sodium hydroxide and hydrofluoric acid etchants. The cost to manufacture this maskant is estimated to be about 50 to 65 percent less than that for currently available chem-mill maskants.
- Electrostatic maskant application techniques can be used effectively with the styrene-butadiene maskant developed under this program and with the Turco 522 styrene-butadiene maskant. Electrostatic techniques cannot be used with neoprene maskants such as Organoceram 1010 because of severe cobwebbing.
- A photoresist technique was developed that can be used to apply chem-mill maskants to titanium substrates. A relatively simple tooling concept was developed to expose to chem-mill maskants internal areas of formed aluminum and titanium alloy skins having bend radii less than two inches.
- An automated, high-pressure water-jet cutting system was used to scribe chem-mill maskants. This system eliminates scratch damage to metal substrates and can be adapted for use with contoured parts.
- Spark testing is an effective technique for detecting pinholes in styrene-butadiene maskants. This technique is not applicable for use with neoprene maskants, however, because of the high conductivity of the maskant material.

2. STUDY AREAS

The following areas of the chem-mill masking and scribing process were investigated in order to reduce costs and increase production rates:

- Develop an improved, low-cost masking system
- Establish improved means of mask application to reduce cost and time
- Develop photo-resist techniques for chem-milling complex titanium shapes
- Develop a practical way to automate scribing of flat parts
- Establish an automated pinhole detection method

3. IMPROVED MASKANT FORMULATION

A vinyl chloride - vinyl acetate copolymer solution resin was formulated with various plasticizers, stabilizers, gelling agents, and solvents to provide a chem-mill maskant suitable for one-coat application.

Additives, in the proper ratios affect polymeric materials in various ways. The basic additives tested with the vinyl chloride-vinyl acetate copolymer and their effect on properties were as follows:

- Plasticizers - These were added to dissolve polyvinyl chloride resin particles to form dispersions or plastisols and to impart flexible properties to the coating.
- Stabilizers - These were added to the coatings because contact with metals can cause oxidation and degradation of plastisol and organosol (solvent solution of plastisol) by dehydrochlorination of the resins. Stabilizers investigated included barium, cadmium and disbutyltin dilaurate.
- Gelling Agents - Cabosil, diglycerides, and monoglycerides were added to increase thixotropy and prevent running of the maskant.
- Solvents - Isopropyl acetate, N - butyl acetate, toluene, and methyl-ethyl ketone were added to the formulation to dissolve the resin and obtain better flow characteristics.

Two basic maskant formulations were initially tested; these are:

- Room Temperature Curing
 - a. 100 parts by weight VYHH resin (Union Carbide)
 - b. Mix (a) with 150 parts by weight toluene
 - c. Mix (b) with 250 parts by weight methyl-ethyl-ketone
 - d. Mix (c) with 5 parts by weight Drapex 4.4 (Argus Chemical)
 - e. Mix (d) with 1.5 parts by weight Stabilizer Mark 275 (Argus Chemical)

• Heat Curing

- a. 100 parts by weight Exon 654 (Firestone)
- b. Mix (a) with 50 parts by weight di (2-ethylhexyl) Phthalate (Union Carbide or Monsanto)
- c. Mix (b) with 10 parts by weight Drapex 4.4 (Argus Chemical)
- d. Mix (c) with 2.5 parts by weight Stabilizer Mark BB (Argus Chemical)

Both formulations were used as starting points for the two systems and were subsequently modified to meet optimum chem-mill maskant requirements. Initial testing of the above formulations showed that both materials had excellent resistance to hot caustic at 190°F. Inspection of the panels after removal from the etchant showed slight etchant seepage under the maskant indicating the need for increased adhesion. To improve this condition a plasticizer adhesive (Kodaflex AD-2) in a ratio of 10 parts by weight was added.

Four basic resin systems were blended with various plasticizers, stabilizers, thickening agents, antioxidants, lubricants, and plasticizer adhesives in an attempt to formulate suitable masking systems. The basic resin systems were polyvinyl acetate (Union Carbide Corporation's VYHH resin), polyvinyl chloride (Firestone's Exon/654 resin), equal parts by weight of VYHH and acrylonitrile, butadiene-styrene (Marbon Chemical Company's Blendex 607 ABS resin), and styrene-butadiene (Shell Chemical Company's Kraton 1101 resin). Seventeen maskant formulations were prepared and tested for such characteristics as chemical resistance, adhesion, temperature resistance, surface continuity, porosity, and ease of scribing and stripping. Results obtained are presented in Table VII. Although the styrene-butadiene Kraton 1101 maskants most closely met the desired performance characteristics, they were further modified to improve adhesion and air-release, and hence reduce porosity (see Table VIII).

The Blendex resin formulations (Maskants 18 and 19) were eliminated from further consideration because minute gel formation during batch preparation would necessitate the introduction of an additional processing step to filter the formulation prior to coating. Previous tests had shown that adhesive properties of the Kraton 1101 resin maskants were degraded by the addition of Cabosil thickening agent. As a result, SP-560 phenolic resin (manufactured by Schenectady Chemicals Incorporated, Schenectady, New York) was substituted for both the Cabosil thickening agent and the Armid "O" lubricant. The resultant Kraton 1101 resin formulations (Maskants 20 and 21) had excellent adhesion and resistance to sodium hydroxide etchant. Nitromethane was added to Maskant 21 to reduce air entrapment during mixing. Although air bubbles were observed on panels coated with Maskant 20, they were not attacked by sodium hydroxide etchant.

Two test panels were coated with Maskant 20 and chem-milled in 4N sodium hydroxide etchant at a temperature of 190°F and at a material removal rate of 1.65 mils per minute per side. A 0.040-inch-deep pocket was chem-milled in one panel (Figure 31). The panel shown in Figure 2-2 was chem-milled in a three-step operation to depths of 0.010, 0.020, and 0.030 inch. Maskant characteristics observed are summarized in Table IX. Test results indicate

NOT REPRODUCIBLE

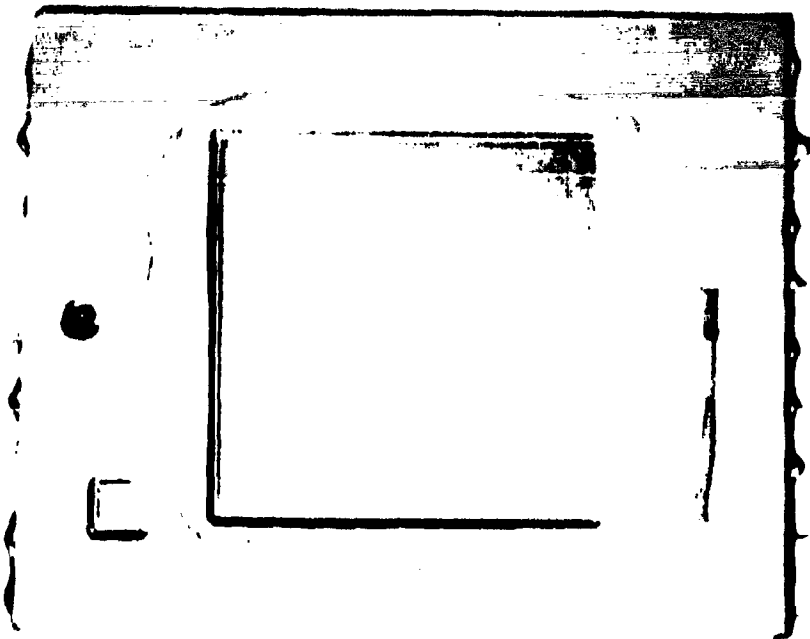


Figure 31 Pocket Chem-Milled in Test Panel Coated with Maskant No. 20

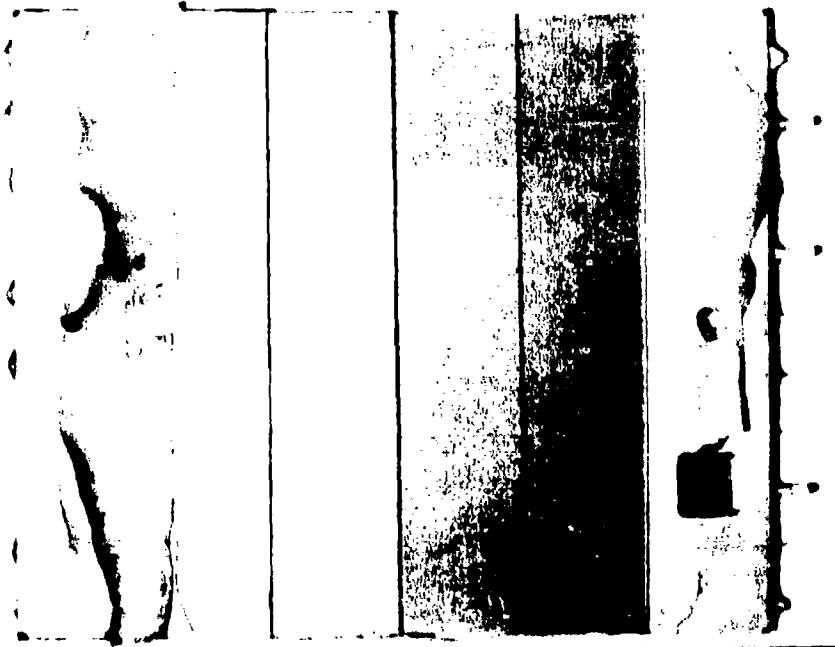


Figure 32 Steps Chem-Milled in Test Panel Coated with Maskant No. 20

Table VII
EVALUATION OF MASKANT 1

| Maskant No. | Basic Resin | Plasticizer | | Stabilizer | | Thickening Agent | Antioxidant | L |
|-------------|-------------------------------------|--------------------|---------------------------------|------------|----------|---------------------|------------------------------|----|
| | | PPH ⁽⁵⁾ | Type | PPH | Type | | | |
| 1. | VYHH ⁽¹⁾ | - | None | - | None | None | None | |
| 2. | Exon 654 ⁽²⁾ | 68 10 | Drapex 7.7 Drapex 4.4 | 2.5 | Mark BB | None | None | |
| 3. | Exon 654 | 50 10 | DOP Drapex 4.4 | 2.5 | Mark BB | None | None | |
| 4. | VYHH | - | None | - | None | None | None | |
| 5. | Exon 654 | 50 10 70 | DOP Drapex 4.4 Drapex 7.7 | 2.5 | Mark BB | None | None | |
| 6. | VYHH | - | None | - | - | None | None | |
| 7. | VYHH | - | None | - | - | None | None | |
| 8. | VYHH | 5 | Drapex 4.4 | 1.5 | Mark 275 | None | None | |
| 9. | VYHH | 5 | Drapex 4.4 | 1.5 | Mark 275 | None | None | |
| 10. | VYHH | 5 | Drapex 4.4 | 1.5 | Mark 275 | None | None | |
| 11. | VYHH | 5 | Drapex 4.4 | 1.5 | Mark 275 | None | None | |
| 12. | VYHH | 5 | Drapex 4.4 | 1.5 | Mark 275 | None | None | |
| 13. | VYHH/Blendex 201 ABS ⁽³⁾ | 5 | Drapex 4.4 | 1.5 | Mark 275 | None | None | |
| 14. | VYHH/Blendex 201 ABS ⁽³⁾ | 5 | Drapex 4.4 | 1.5 | Mark 275 | None | None | |
| 15. | Kraton 1101 ⁽⁴⁾ | - | None | - | None | None | Plastinox LTOP/ 330 Ethyl | Ar |
| 16. | Kraton 1101 | - | None | - | None | Atlas-Chem G-695 | Plastinox LTOP/ 330 Ethyl | Ar |
| 17. | Kraton 1101 | - | None | - | None | Cabosil | Plastinox LTOP/ 330 Ethyl | Ar |

(1) Polyvinyl acetate (Union Carbide Corporation)

(2) Polyvinyl chloride (Firestone)

(3) Equal Parts by weight

(4) Styrene-butadiene (Shell Chemical Company)

(5) PPH - Parts Per Hundred

PPW - Parts by Weight

A

FORMULATIONS

| Lubricant | Plasticizer Adhesive | | Solvent | | Cure Cycle | Porosity Test Results | Adhesion |
|-----------|----------------------|---------------|--------------------|-----------------------|---|--------------------------|--------------|
| | grams | Type | PBW ⁽⁶⁾ | Type | | | |
| None | - | None | 150 250 | Toluene MEK | Room temperature | Fair-Good | Poor |
| None | 5 | Kodaflex AD-2 | - | None | 250°F. for 15 minutes | Fair-Good | Poor |
| None | 5 | Kodaflex AD-2 | - | None | 250°F. for 15 minutes | Fair-Good | Poor |
| None | 20 | Kodaflex AD-2 | 150 250 | Toluene MEK | Room temperature | Fair-Good | Good |
| None | 10 | Kodaflex AD-2 | - | None | 250°F. for 15 minutes | Fair-Good | Poor |
| None | 10 | Kodaflex AD-2 | 150 250 | Toluene MEK | Room temperature | Fair-Good | Fair |
| None | 10 | Kodaflex AD-2 | 150 250 | Toluene MEK | RT for 16 hours; post-cure at 175°F, 200°F, 275°F for 30 mins. | Fair-Good | Poor |
| None | 5 | Kodaflex PA-3 | 150 250 | Toluene MEK | RT for 16 hours; post-cure at 180°F and 275°F. for 30 mins. | Fair-Good | Poor |
| None | 50 | Kodaflex PA-3 | 150 250 | Toluene MEK | RT for 16 hours; post-cure at 180°F and 275°F. for 30 mins. | Fair | Poor |
| None | 75 | Kodaflex PA-3 | 150 250 | Toluene MEK | RT for 16 hours; post-cure at 175°F and 285°F. for 30 mins. | Fair-Good | Poor |
| None | 150 | Kodaflex PA-3 | 150 250 | Toluene MEK | RT for 16 hours; post-cure at 175°F and 285°F. for 30 mins. | Fair | Did not peel |
| None | 100 | Kodaflex PA-3 | 150 250 | Toluene MEK | RT for 16 hours; post-cure at 175°F and 285°F for 30 mins. | Fair | Fair |
| None | 100 | Kodaflex PA-3 | 150 250 | Toluene MEK | None | - | - |
| None | - | None | 200 250 | MEK Cyclohexanone | RT for 16 hours; post-cure at 145°F and 250°F for 30 minutes | - | Poor |
| Unmed "O" | - | None | 200 300 | Xylene VMSP Naptha | RT for 16 hours; post-cure at 150°F. for 30 minutes | Good | Good |
| Unmed "O" | - | None | 200 300 | Xylene VMSP Naptha | RT for 16 hours; post-cure at 150°F for 30 minutes | Good | Poor |
| Unmed "O" | - | None | 200 300 | Xylene VMSP Naptha | RT for 16 hours; post-cure at 150°F for 30 minutes | Good | Poor |

B

EVALUATION OF MOD13

| Maskant No. | Base Resin | | Plasticizer | | Stabilizer | | Antioxidant | |
|----------------|------------|--------------------|-------------|-------------------|------------|----------|-------------|---------------------------------|
| | pbw* | Type | pbw | Type | pbw | Type | pbw | Type |
| 18 | 100 | Blendex 607 ABS | 5 | Santicizer 140 | 1.5 | Mark 275 | — | None |
| 19 | 100 | Blendex 301 ABS | 5 | Santicizer 140 | 5.0 | Mark 275 | — | None |
| 20 | 100 | Kraton 1101 SB | — | None | — | None | 0.3 0.3 | Ethyl 330 Plastinox IITDP |
| 21 | 100 | Kraton 1101 SB | — | None | — | None | 0.3 0.3 | Ethyl 330 Plastinox IITDP |

*pbw = parts by weight

A

TABLE VIII
 DIFIED MASKANT FORMULATIONS

| Adhesive | | Solvent | | Air Release Agent | | Cure Cycle | #5 Zahn Cup Viscos- ity, sec | Observations |
|----------|--------------------|------------|---|-------------------|-------------------|---|------------------------------------|--|
| pbw | Type | pbw | Type | Grams | Type | | | |
| - | None | 400 | MEK | - | None | RT for 16 hours; 250°F for 1/2 hour | 8 | Minute gel formation; no further testing |
| 5 | SP-553 | 700 | MEK | - | None | RT for 16 hours; 250°F for 1/2 hour | 11 | Poor Adhesion |
| 5 | SP-560 Phenolic | 200 300 | Xylene VM&P Naptha | - | None | RT for 16 hours; 250°F for 1/2 hour | 65 | Excellent adhesion and resis- tance to NaOH etchant |
| 5 | SP-560 Phenolic | 200 300 | Xylene VM&P Naptha plus 126grams MEK | 136 | Nitro- methane | RT for 16 hours; 250°F for 1/2 hour | 18 | Excellent adhesion and resis- tance to NaOH etchant |

that the Kraton 1101-based maskants should be reinforced with pigment to improve peelability and etch-line definition and that they are resistant to acid etchants including hydrofluoric acid.

TABLE IX
CHARACTERISTICS OF MASKANT NO. 20

| CHARACTERISTIC | PERFORMANCE | REMARKS |
|--|-------------|--|
| Resistance to Sodium Hydroxide Etchant | Excellent | No pinholes on panel surface; Some breaks at corners and edges |
| Adhesion to Aluminum | Excellent | |
| Scribability | Excellent | No beading of resin during cutting operation |
| Peelability | Good | Maskant is elastic; it will be less acceptable to shop operations than a reinforced maskant system |
| Etch-Line Definition | Fair | Maskant softens non-uniformly along cut edge so that a straight line is not always obtained |
| Self Sealing of Step Scribe Line | Good | |

An attempt was made to improve the mechanical strength of styrene/butadiene-based chem-mill maskant formulations. Two approaches were examined -- incorporation of pigments such as magnesium silicate and colloidal silica, and variation of the solvent system. To reduce the incidence of air entrapment during mixing and coating operations, the following techniques were evaluated:

- Addition of air-release agents such as nitromethane
- Substitution of lower molecular weight styrene-butadiene copolymer
- Reduction of viscosity

The chemical composition of the formulations developed are summarized in Table X. Basic Formulation Number 20 was modified by replacing 10 and 20 percent of the solvent with technical grade magnesium silicate. The resultant formulations (Numbers 23 and 24) were applied to titanium and aluminum; they showed a significant improvement over Formulation 20 in ease of removal and reduced elasticity.

TABLE X

COMPOSITION OF CHEM-MILL MASKANT FORMULATIONS

| Formula Component | Percent By Weight Composition | | | | | | | | | | |
|-----------------------------------|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 20 | 23 | 24 | 25 | 26 | 27 | 27a | 28 | 28c | 29 | 30 |
| Kraton 1101 | 16.52 | 16.52 | 16.52 | - | 16.52 | 15.27 | 15.27 | 15.27 | 15.27 | 15.27 | 15.27 |
| Kraton 1102 | - | - | - | 16.52 | - | - | - | - | - | - | - |
| Phenolic Resin S.P. 560 | 0.83 | 0.83 | 0.83 | 0.83 | 0.83 | 0.77 | 0.77 | 0.77 | 0.77 | 0.77 | 0.77 |
| Anti-Oxidant Ethyl 330 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| UV Absorber Plastinox LTDP | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Talc (Magnesium Silicate) | - | 10.00 | 20.00 | - | - | 13.86 | 13.86 | - | - | 13.86 | 13.86 |
| Cab-O-Sil (Silica) | - | - | - | - | - | - | - | 5.00 | 5.00 | - | - |
| Air Release Agent Nitromethane | - | - | - | - | - | - | - | - | 5.00 | 5.00 | - |
| Xylene | 33.02 | 29.02 | 25.02 | 33.02 | - | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 |
| VM&P Naphtha | 49.53 | 43.53 | 37.53 | 49.53 | 16.51 | 56.00 | 55.24 | 64.86 | 59.86 | 51.00 | 55.24 |
| Methyl-Ethyl- Ketone | - | - | - | - | 66.04 | - | - | - | - | - | - |
| Plasticizer Drapex 4.4 | - | - | - | - | - | - | 0.76 | - | - | - | - |
| Drapex 7.7 | - | - | - | - | - | - | - | - | - | - | 0.76 |
| Total Solids | 17.45 | 27.45 | 37.45 | 17.45 | 17.45 | 30.00 | 30.76 | 21.14 | 21.14 | 30.00 | 30.76 |

Formulation 24 provided very good line-definition during etching and a minimum amount of entrapped air. Longer drying periods were required between successive coating applications, however, because of the high viscosity of this formulation. In addition, the cured material tended to break during the peeling operation.

In order to increase elasticity, Formulation Number 25, which contained Kraton 1102, was evaluated as a substitute for Kraton 1101. Although both polymers are similar in composition, Kraton 1102 has a shorter polymeric chain length and lower molecular weight (characteristics favorable to a lower viscosity formulation). The increased elasticity of the cured coating, however, rendered the use of Kraton 1102 impractical for the subsequent scribe and peel operation.

In Formulation Number 26, the solvent blend was varied to reduce the coating elasticity. Methyl-ethyl-ketone (MEK) is a good solvent for the thermoplastic (polystyrene) phase of the resin but a poor solvent for elastomeric (polybutadiene) phase. Thus, Formulation 26 represents an effort to reduce the elastomeric influence of the Kraton 1101 resin. The objective of the test was achieved but at the expense of increased mixing time and poorer etchant resistance.

In Formulation Number 27 the solvent content was increased in order to reduce viscosity and shorten drying time. Optimum performance characteristics were obtained with this formulation at a 30 percent total solids content.

The use of colloidal silica (Cab-O-Sil) instead of talc (magnesium silicate) was evaluated in Formulations 28 and 28A. Flow rate across the substrates and coating thickness were non-uniform. Numerous air bubbles developed on the coated panel; this condition grew worse with each successive coat. Formulation 28A incorporated nitromethane as an air-release agent. Although the number of occlusions was considerably reduced, they were not completely eliminated.

Formulation 27 was selected as having the optimum physical characteristics necessary to perform well as a chem-mill maskant. Its ratio of polymer to filler (Kraton 1101/talc) is between those of Formulations 23 and 24. This would predict a coating solution viscosity of 92.5 seconds and a total solids content of 32.45 percent. By reducing the total solids content to 30 percent without altering the ratio of polymer to filler, a viscosity of 40 seconds was achieved. The resulting coating had very few air occlusions and was well within the range of optimum coating thickness. Coated panels of titanium and aluminum were chem-milled and showed very good etchant resistance after being cured at 250°F for 1/2 hour.

Room temperature-cured panels exhibited good resistance to sodium hydroxide etchant for aluminum but poor resistance to hydrofluoric acid etchant for titanium. In the latter case, severe lateral etching took place at the maskant/titanium interface to a distance of one inch from the chem-mill line. The addition of an air release agent such as nitromethane Formulas 28A and 29 did not reduce the number of air occlusions in cured dip coatings. When test panels were coated by flow coating techniques instead of by immersion, however, very smooth and uniform maskant surfaces were obtained. Plasticizers were evaluated in Formula 27 to further improve the sharpness and accuracy of the chem-mill line and the smoothness of the chem-mill pocket wall. A polymeric epoxidized polyester (Drapex 7.7) and an octyl epoxy tallate were added at five percent by weight of the Kraton 1101 (Formulas 27A and 30). The latter proved to be very effective as illustrated in Figures 31 and 32. Comparative coating thickness data are presented in Table XI.

TABLE XI
MASKANT COATING THICKNESSES

| Maskant Material | Thickness, mils per side | Number of Coats |
|------------------|-----------------------------|-----------------|
| Organoceram 1010 | 14-17 | 4 |
| Turco 522 | 15 | 3 |
| Formula 27 | 10-11 | 4 |
| Formula 27a | 10-12 | 4 |

Forty gallons of Formula 27 were manufactured by Berco Industries, Westbury, New York, using standard production equipment. This maskant meets all performance requirements for a chem-mill maskant with respect to smoothness and uniformity of coating surface, scribe and peel characteristics, and resistance to sodium hydroxide and hydrofluoric acid etchants. Manufacturing costs have been estimated to be 50-65 percent less than that for presently available commercial products.

A summary of the physical characteristics and general performance of the formulations studied is given in Table XII. Laboratory observations have indicated that an acceptable chem-mill maskant must meet the following criteria:

- Yield a sharp, clean cut under moderate pressure applied manually during a single pass of the scribing tool.
- Release easily from metal surfaces after scribing.
- Remain continuous during the peeling operation.

Thus far, it has been observed that these criteria are best met by a coating thickness within the range of 8 to 12 mils. Thinner coatings adhere too strongly to the metal surfaces and break easily during the peeling operation. Thicker coatings are difficult to scribe.

4. IMPROVED APPLICATION TECHNIQUES

The most widely used methods of applying maskants are flow-coating and dipping. These are manual operations and results are based on operator skill. The nature of the operation allows air entrapment which causes pinholes and porosity.

The application of maskants by airless electrostatic spraying was studied. This process involves the charging of the panels to be masked and the airless atomizing of the maskant material, which is dispersed by a revolving disc (Figure 33) and attracted to the panels. Electrostatic spraying, if automated as shown in Figure 34), could significantly reduce chem-mill masking costs.

The Ransburg Electro-Coating Corporation of Indianapolis, Indiana, electrostatically coated 7 x 5.5-inch, 7075-T6 aluminum alloy panels with Turco 522 and Organoceram 1010 maskants using a 20-inch-diameter disc (reciprocating/tilted) rotating at a speed of 1,800 revolutions per minute. The

TABLE XII
PHYSICAL CHARACTERISTICS OF CHEM-MILL MASKANTS

| Form No. | Visc,* sec | Thick, mils | Coats | Coating Appearance | Performance | | |
|----------|------------|-------------|-------|---|-------------------------------|--|--------------------|
| | | | | | Scribe | Peel | Etchant Resistance |
| 20 | 30 | 7.5 | 3 | Clear - Uniform; Air Occlusions | Good | Too Elastic | Good |
| 23 | 85 | 12.5 | 3 | Translucent; Excessive Air Occlusions | Good | Less Elastic Than #20 | Fair |
| 24 | 100 | 14.5 | 3 | Opaque; Numerous Air Occlusions | Good | Breaks Too Easily | Very Good |
| 25 | 15 | 5 | 3 | Clear; Fewer Air Occlusions Than #20 | Good | More Elastic Than #20 | Good |
| 26 | 180 | 13 | 3 | Translucent; Numerous Air Occlusions | Good | Elasticity Equal to #23 | Fair |
| 27 | 40 | 10 | 4 | Opaque; Fewer Air Occlusions Than #25 | Good | Acceptable | Very Good |
| 27A | 40 | 11 | 4 | Opaque; Fewest Air Occlusions in series | Good | Acceptable | Very Good |
| 28 | 60 | 10.5 | 2 | Translucent; Excessive Air Occlusions | Requires Heavy Knife Pressure | Difficult; Adheres Strongly to Substrate | Very Good |
| 28A | 60 | 16 | 3 | Translucent; Few Air Occlusions | Equal to #28 | Equal to #28 | Very Good |
| 29 | 46 | 10 | 3 | Same as 28A | Good | Acceptable | Very Good |
| 30 | 7.5 | 8 | 4 | Opaque; very few Air Occlusions | Good | Difficult | Very Good |

*Zahn No. 5 Viscometer

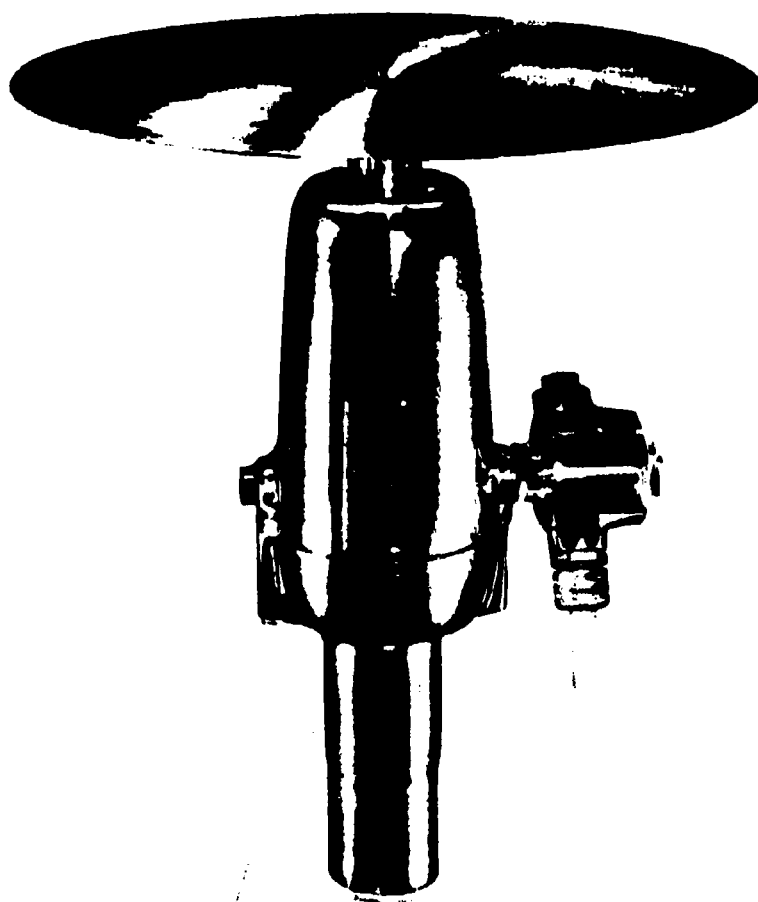


Figure 33 Electrostatic Disc Atomizer for Maskant Application

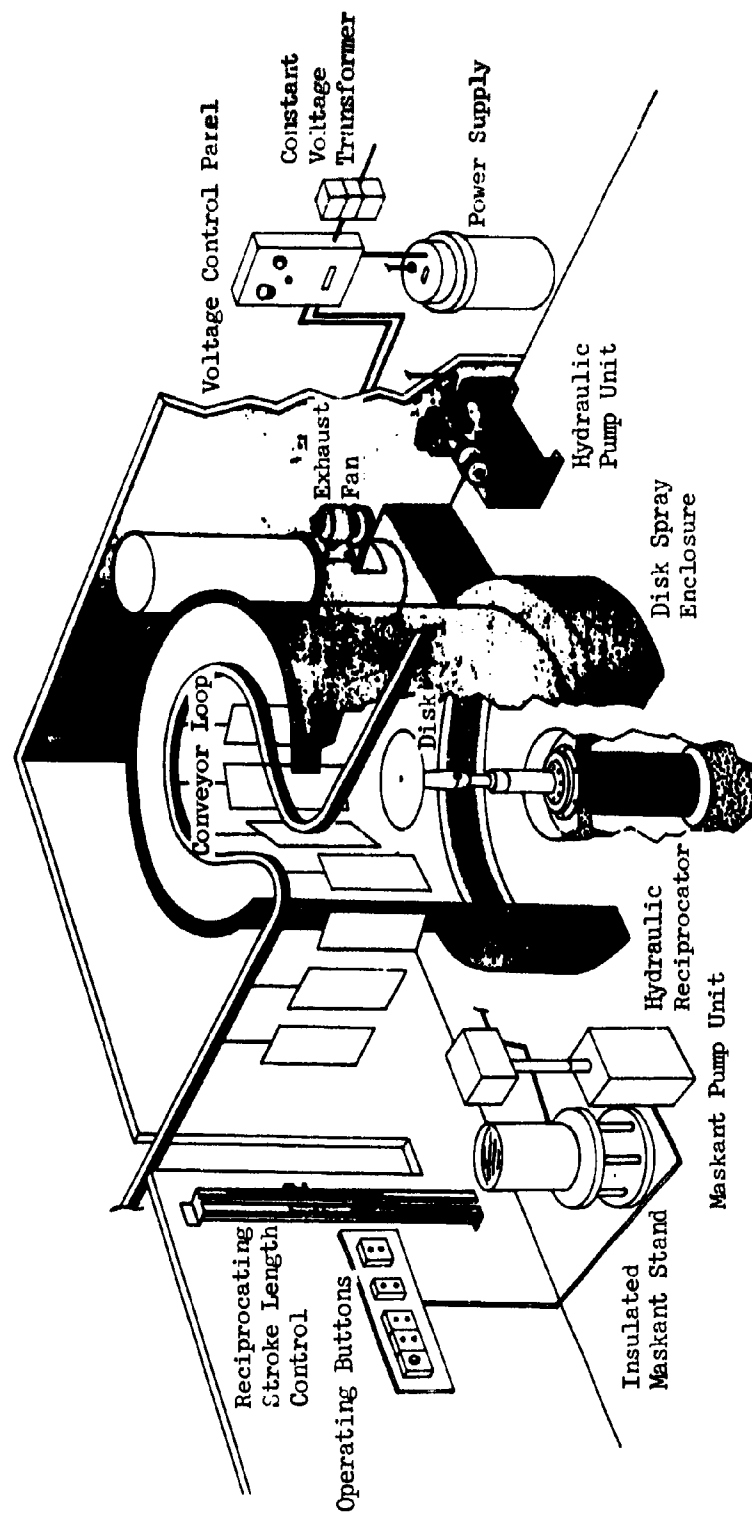


Figure 34 Fully Automated Electrostatic Spray System for Maskant Application

overhead-mounted reciprocator had a maximum stroke of 30 inches and operated at a frequency of 10 cycles per minute. The conveyor speed was set at 7.5 feet per minute. The Turco 522 maskant was thinned down with a 50/50 percent toluol/xylol solvent mixture to a Ford Cup #4 viscosity of 66 seconds. The Organoceram 1010 maskant was thinned down with a 50/25/25 percent toluol/xylol/butyl cellulose solvent mixture to a Ford Cup #4 viscosity of 40 seconds. The maskants were electrostatically applied at a rate of 500 cubic centimeters per minute per loop and then cured at 250°F for 45 minutes.

Difficulty was encountered in electrostatically applying the Organoceram 1010 maskant. Severe cobwebbing occurred. Panels suitable for testing could not be produced. Adequate maskant buildup, however, was obtained with the Turco 522 material. Panels that were passed two, four, and six times through the conveyor loop had maskant buildups of 0.0025, 0.0050/0.0040, and 0.0089 inch, respectively. The test panel with the 0.0025-inch-thick Turco 522 coating failed a 4,000-volt spark test. The other three panels passed a 10,000-volt spark test without arcing.

A possible racking arrangement for typical aircraft parts scheduled for electrostatic maskant spraying is shown in Figure 35. The percentage distribution of part sizes that could reasonably be expected to be masked and chem-milled is also shown in Figure 35.

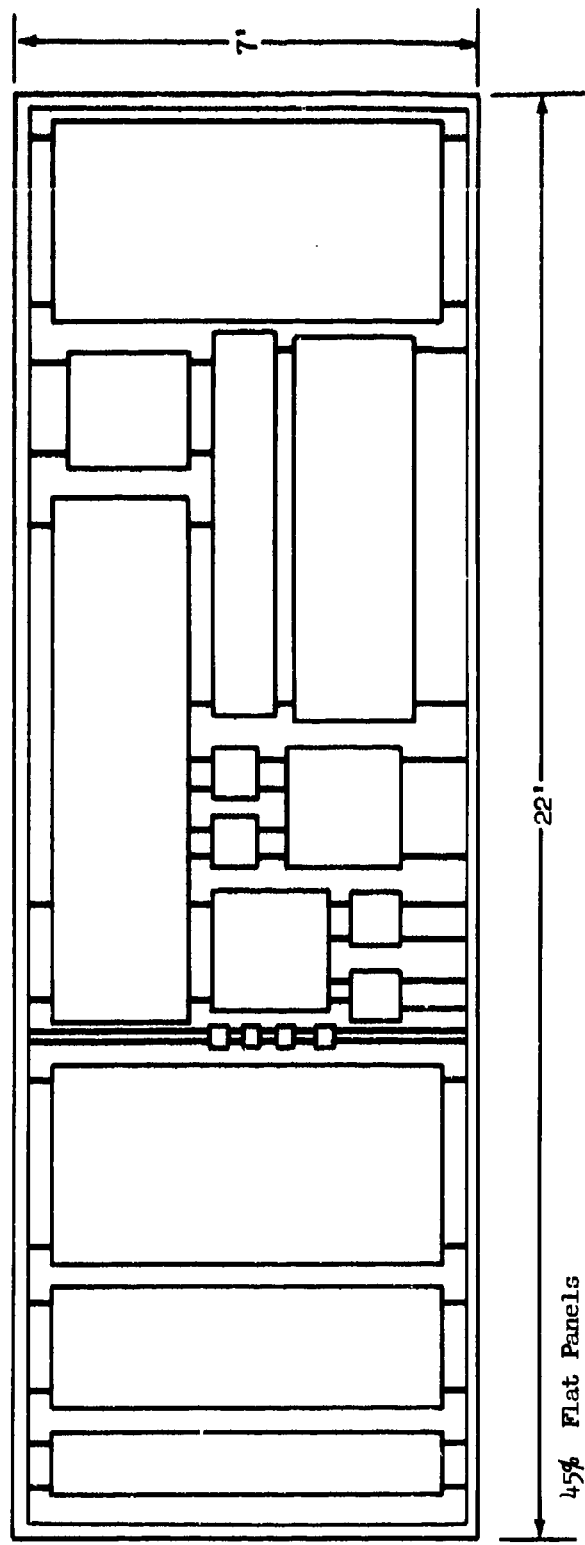
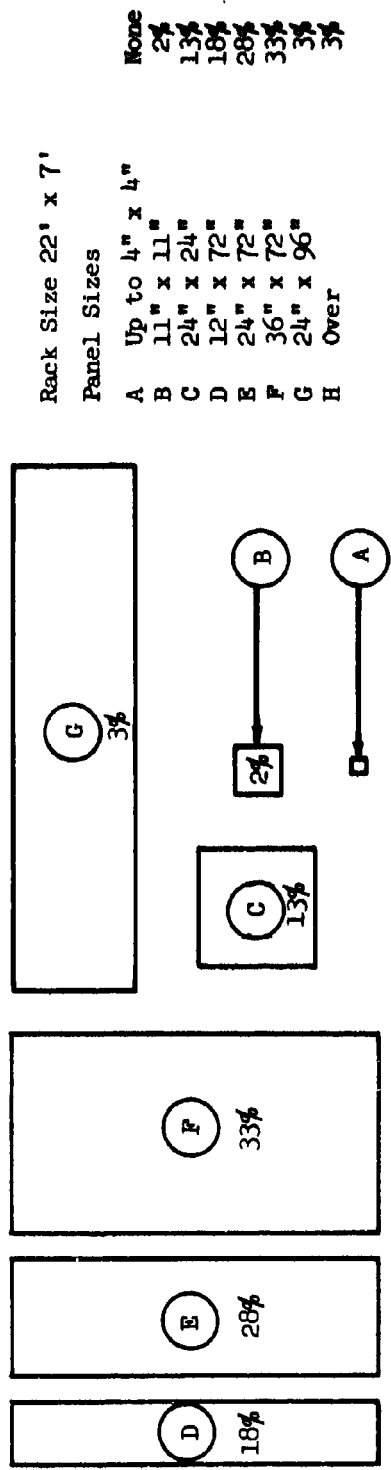
A pilot study was also performed by the Ransburg Electro-Coating Corporation to determine the performance characteristics of Formula 27 when applied by electrostatic deposition techniques. Because the evaporation rate of the Formula 27 solvent blend was too high for this type of coating application, three parts of a high-boiling solvent blend had to be added to five parts of maskant in order to produce a smooth coating surface and to prevent "cobwebbing" during spraying. The dilutions tested are shown in Table XIII.

TABLE XIII

MASKANT FORMULA 27 DILUTIONS TESTED ELECTROSTATICALLY

| Maskant Dilution Component | Composition, Parts by Volume | | |
|----------------------------|------------------------------|------|------|
| | I | II | III |
| Formula 27 | 5 | 5 | 5 |
| Toluene | 0.75 | 0.75 | 0.75 |
| Methyl Isobutyl Ketone | 0.75 | - | - |
| Methyl Ethyl Ketone | - | 0.75 | 0.75 |
| Solvesso 100* | 1.50 | - | 0.75 |
| Solvesso 150* | - | 1.50 | 0.75 |

* (Proprietary hydrocarbon blend)



- 45% Flat Panels
- 50% Contour Shapes Ranging in Radius From 10 to 40 Inches
- 4.5% Channel Shapes
- 0.5% Tubing Ranging in Diameter From 0.5 to 3 Inches

Figure 35 Typical Chem-Milling Part Sizes for Fighter-Type Aircraft and Racking Arrangement for Electrostatic Spray System

Composition III, which proved to be the most satisfactory, was applied in one, two, and three passes through the coating line. Coating thicknesses of 1.75, 2.00 and 6.00 mils per side were obtained for one, two and three passes, respectively. The six-mil-thick coating was the only one deemed suitable for subsequent scribe and peel operations.

Although maskant was applied to only one side of each panel, about 0.5 mil of maskant was also deposited on the opposite side of each panel as a result of "wrap-around." Since the applied voltage establishes an electrostatic charge over the entire panel surface, a small amount of the material being sprayed is attracted to the side of the panel away from the nozzle as the sprayed maskant approaches the panel to be coated. When both sides of a part are passed through an S-shaped coating line, therefore, the coating thickness builds up as a result of material emitted by the spray nozzle as well as from "wrap-around." A coating thickness of ten mils per side could be expected after four passes through an S-shaped conveyor line.

Electrostatic spray coating can be basically considered as a single-application technique. Parts need be racked only once, since part rotation (required with flow-coating systems) is not necessary. Once the parts have been racked, they can be passed automatically through the line as many times as is necessary to build up the desired coating thickness. Comparative material usages for the electrostatic and flow-coating methods are given in Table XIV.

TABLE XIV

MATERIAL USAGES FOR ELECTROSTATIC AND FLOW-COATING TECHNIQUES

| Maskant System | Application Technique | Coating Thickness, mils per side | Usage for Two-side Coverage, square feet per gallon |
|------------------|-----------------------|----------------------------------|---|
| Formula 27 | Electrostatic | 6 (exp) | 22.0 |
| Formula 27 | Electrostatic | 10 (theor) | 16.2 |
| Organoceram 1010 | Flow-Coating | 10 | 33 4 |
| Turco 522 | Flow-Coating | 10 | 40.0 |

The poor efficiency of material usage with the electrostatic method is offset by the lower material cost of Formula 27 and reduced manpower requirements.

5. PHOTOFABRICATION

Photosensitive maskants offer an opportunity to execute difficult chem-mill tasks. Control surfaces with bend radii less than two inches cannot be scribed and stripped when masked with conventional chem-mill masks. Foil and thin gauge (0.015 inch and less) skins are susceptible to distortion during manual maskant removal or subsequent routing operations. Man-hours for scribing many small components can be reduced by the photofabrication process, since a single transparency can be used to fabricate several small parts at the same time. Photoetching was investigated for its applicability in the following areas:

- Fabrication of Leading Edge Members with Bend Radii Less than Two Inches - Presently, aluminum parts with less than a two-inch bend radius must be masked and scribed flat and then formed. This method, however, cannot be applied to titanium alloys because they require high forming temperatures that prohibit the use of maskants prior to forming.
- Chem-Milling of Aircraft Surfaces Less than 0.015 Inch Thick - Bends and wrinkles produced on thin-gauge skins during the process of removing conventional maskants from thin chem-milled skins will be eliminated by using photosensitive masks which can be removed easily by immersion in the proper solvent.

Chem-milling is an inexpensive metal-removal technique used by the aircraft industry chiefly to meet minimum weight requirements for high-speed aircraft. Ordinarily this is accomplished by chem-milling a pattern of rectangles (pockets) of dimensions designed to remove a known volume of material. For titanium flat stock and simple contours, scribe and peel maskants are adequate for establishing the chem-mill pattern. They cannot, however, be used for complex contours because of the following:

- If the flat stock is masked and scribed prior to forming, the maskant material deteriorates at the temperatures required for titanium forming.
- If a contoured part is masked after forming, scribing is difficult or impossible to accomplish on the interior surfaces.

For these reasons, photoresist maskants were investigated for use in chem-milling the internal surfaces of formed parts.

Photofabrication is a process whereby a solution of light-sensitive polymer (photoresist) is applied to a metal surface and heat-cured to provide a uniform solid coating on the metal. The coated metal (contoured part or flat stock) is then placed between a set of matched photographic transparencies bearing an opaque design corresponding to the desired chem-mill pattern. Vacuum is applied to establish intimate contact between the transparencies and the coated part. The entire assembly is then subjected to ultraviolet radiation for a specific time period. Where the radiation is transmitted through the clear areas of the transparency to the coating underneath, it further hardens (polymerizes) the polymer. That part of the coating under the opaque areas of the tooling is not affected and

remains in its heat-cured condition. The light-exposed, coated part is then immersed (developed) in a suitable solvent that removes only that part of the polymer coating that was not subjected to ultraviolet radiation. Finally, the part is placed in a solution that dissolves the exposed metal but does not attack the light-hardened polymer.

An investigation into this type of metal removal was conducted under a Grumman funded advanced development program in 1969 (see Grumman Report No. AD808-11-69.1). Satisfactory tooling for formed aluminum parts was developed from clear, flexible, vacuum-formed polyvinyl chloride (PVC) sheet. Rigid opaque PVC sheet was bonded to the interior of the female tool to provide the chem-mill pattern. A vacuum line fitting was welded into the corner of the tool so that a vacuum seal between the tool and the aluminum part could be maintained during light activation (Figure 36). The principles of this experimental tooling approach were adapted to meet the requirements for chem-milling the interior surface of a wing leading edge configuration, as follows:

- Formed aluminum (Figure 37) was used as a master part to build a lightweight fiberglass drill jig for tooling holes so that each part would be accurately aligned within the vacuum masking tool.
- Lightweight fiberglass frames replaced the cast aluminum frames used in the original vacuum tool.
- Rigid opaque PVC formed to the contour of the master was cut to the dimensions required for chem-mill pockets and temporarily bonded to the interior surface of the master part with rubber cement.
- Transparent, flexible, UV-stable PVC sheet was then vacuum-formed at 250-300°F onto the master part. Vacuum grooves were also formed during this step.
- After the system had cooled, the transparent PVC forms were removed and PVC adhesive applied to the opaque PVC pattern. The transparent forms then were returned to the master part and vacuum applied to effect a permanent bond with the opaque material.
- The temporary bond between the master part and the opaque PVC was then removed.
- Clear plexiglass tooling pins were bonded to the finished reusable chem-mill masking tool.

A sketch of the tool that was fabricated is shown in Figure 38. The following commercially available photoresists were evaluated to determine their optimum UV exposure characteristics and resistance to hydrofluoric acid:

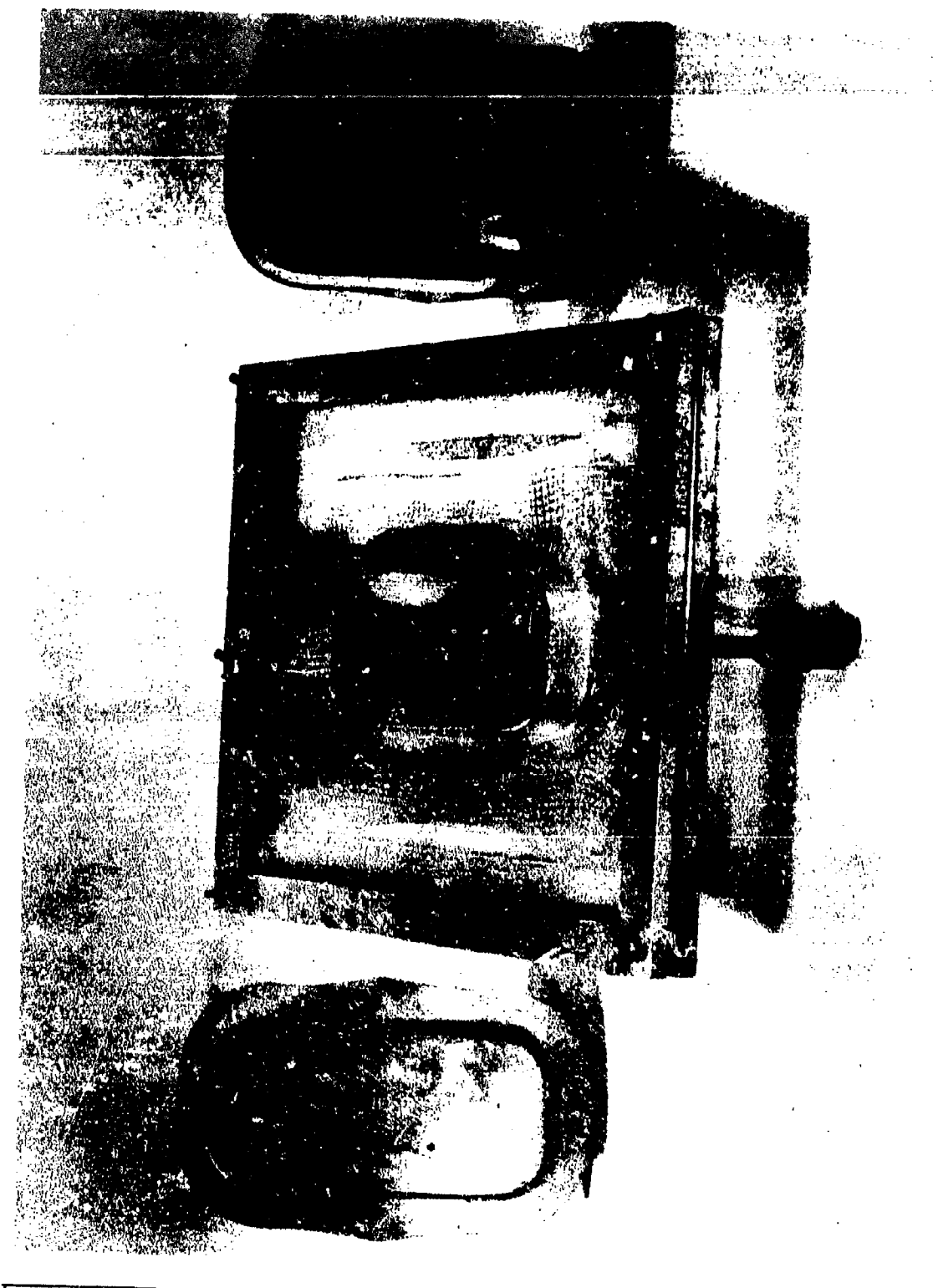


Figure 36 Clear Polyvinyl Chloride (PVC) Photographic Tooling

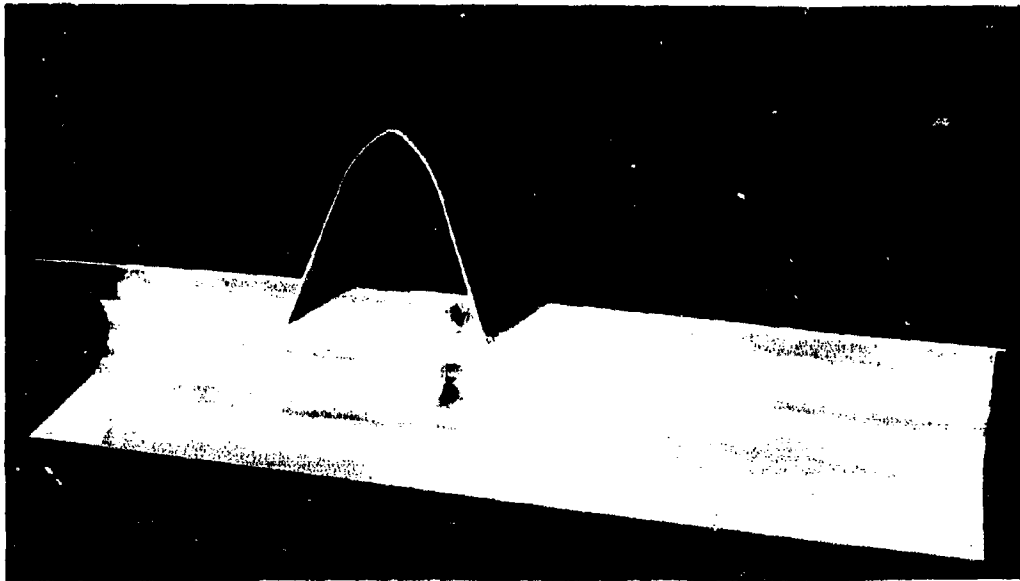


Figure 37 Formed Aluminum Alloy Leading Edge Test Panel

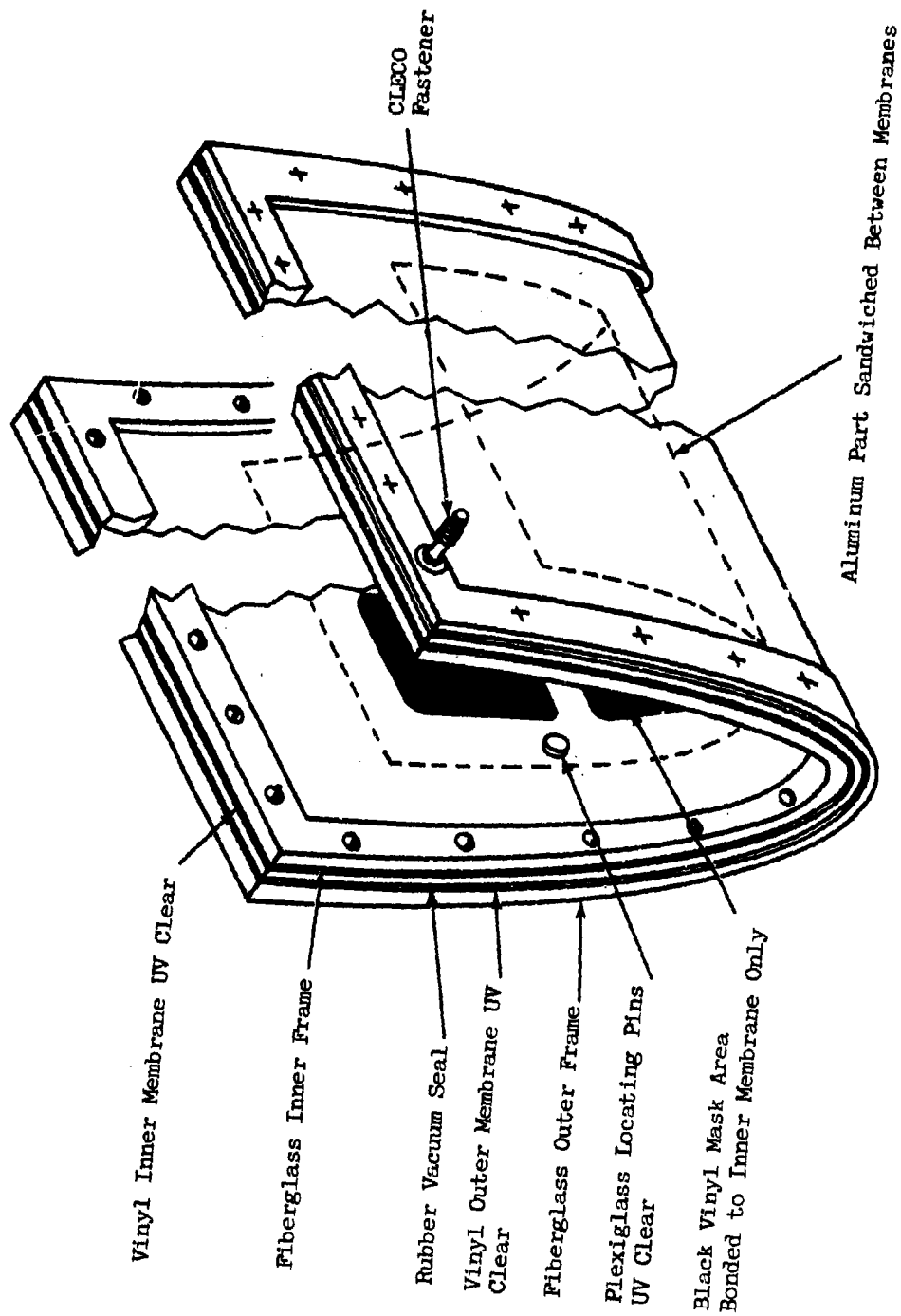


Figure 38 Photographic Tool for Leading Edge Configuration

- KMER - Eastman Kodak Co.
- KPR - Eastman Kodak Co.
- CMR-5000 - Dynachem Corp.
- Waycoat PF - Philip S. Hunt Chemical Corp.

For this work the source of ultraviolet radiation was a pair of water-cooled, high-pressure mercury vapor lamps manufactured by Colight, Incorporated (Figure 39). The photoresist coated part/vacuum tool assembly was suspended in the center of the movable frame positioned between the two lamps. Part of the parallel radiation from the lamps was diverted in four directions to aid in reducing shadow effects on irregularly shaped parts, for example, the type of configuration illustrated in Figure 37. Shadow effects were not expected to be a problem with the leading edge contour but may be a problem with other parts.

Initial test results indicated that Waycoat PF and Dynachem CMR-5000 photoresists are more resistant to hot, aqueous hydrofluoric acid (titanium) etchant than Kodak KMER photoresist. The following criteria were used to evaluate photoresist performance:

- Ease of coating application
- Degree of adhesion of coating to metal substrate
- Line definition after exposure to ultraviolet radiation through plastic tooling
- Economic time requirement for ultraviolet radiation exposure
- Ease of pattern development
- Pinhole resistance in ten percent by volume hydrofluoric acid at 100 - 110°F
- Ease of stripping photoresist coating from metal substrate after chem-milling.

Although performance of the Waycoat PF and Dynachem CMR-5000 photoresists with aluminum and titanium substrates was about equivalent, resistance of the photoresists to ten percent by volume hydrofluoric acid became poor after 20 minutes immersion at 110°F.

Preliminary aircraft wing leading-edge configurations were formed from 7075-T6 aluminum alloy sheet because of the low cost, ready availability, and ease of fabrication. The formed 7075-T6 aluminum alloy parts and flat Ti-6Al-6V-2Sn titanium alloy panels were coated with the Waycoat PF and Dynachem CMR-5000 photoresist systems and evaluated.



Figure 39 Water-Cooled, High-Pressure Mercury Vapor Lamps

The structural simplicity of the formed aluminum parts made it possible to use dip coating to apply the photoresists. It was, therefore, not necessary to evaluate spray or flow coating processes at this time. When multiple photoresist coatings were applied to a single test panel, each application was begun from a different edge of the panel to insure uniform coating thickness. The rate of panel withdrawal from the coating solution determined coating thickness. Panel withdrawal rates of 12 and 24 inches per minute gave coating thicknesses of 0.3 and 0.5 mil per side per single application, respectively, for each photoresist. Immediate panel withdrawal gave a coating thickness of 1.0 mil per side per single application for each photoresist. Each photoresist used in the single-application tests was in an undiluted condition as received from the manufacturer.

After maximum light activation (five minutes) and subsequent development, the single-coat approach was abandoned because coating coverage along the panel edges was insufficient to withstand prolonged etchant immersion. Solvent entrapment in multiple coatings of undiluted photoresists led to insufficient light activation which, in turn, caused poor pattern development. Solvent entrapment in photoresist coatings thicker than one mil inhibits crosslinking of the photoresist polymer chains during exposure to ultraviolet radiation, thereby lowering the polymer's resistance to the developer solvent. Curing of the photoresist coatings at higher than recommended temperatures prior to light activation did not alleviate the problem. Exposure to ultraviolet radiation for periods longer than five minutes was deemed impractical for economical production processing. As a result, the photoresists used in succeeding tests were diluted 20 percent with thinner solvent (four parts of undiluted photoresist to one part of thinner solvent). Although good pattern development was obtained with four-coat application of diluted photoresist, the coating build-up along the panel edges led to the same poor pattern development encountered previously. A reduction in the number of applications from four to two eliminated this problem.

The photoresist manufacturers recommended that the photoresist coatings be oven-cured within a temperature range of 180 - 200°F for 10-15 minutes prior to light activation to remove residual solvent. A study was made of the effect of longer curing times and higher curing temperatures on resistance of photoresists to attack by hydrofluoric acid etchants. The Waycoat PF and Dynachem CMR-5000 photoresists were diluted 20 percent with thinner solvent to a Zahn No. 1 cup viscosity of 50 ± 5 seconds at 72 ± 3°F. Two photoresist coatings were applied to each test panel. The first and second coatings were started from opposite ends of the panel. The first photoresist coating was allowed to dry for 10 minutes at ambient air temperature before the second coating was applied. The coated panels were oven-cured after application of the second coating. The test results summarized in Table XV are somewhat inconclusive. The photoresist manufacturers claimed that curing temperatures above 250°F rendered the coatings resistant to attack by developer solvent.

TABLE XV

**EFFECTS OF CURING TIME AND TEMPERATURE ON RESISTANCE
OF PHOTORESIST COATINGS TO ATTACK BY HYDROFLUORIC ACID**

| Curing Cycle | | Number of Pinholes After One-Hour Immersion In Hydrofluoric Acid Etchant | |
|--------------|------------|--|-------------------|
| Temp., °F | Time, min. | Waycoat PF | Dynachem CMR-5000 |
| 185 | 20 | Numerous | Numerous |
| 250 | 10 | Numerous | Four |
| 250 | 15 | Three | Numerous |

Exposure to ultraviolet radiation for time periods longer than five minutes did not improve resistance of the cured photoresist coatings to attack by hydrofluoric acid etchant. Data obtained are presented in Table XVI. Although Dynachem CMR-5000 photoresist had greater initial resistance to HF attack, overall performance of both photoresist materials was about equal.

TABLE XVI

**EFFECTS OF ULTRAVIOLET RADIATION
EXPOSURE TIME ON RESISTANCE OF PHOTO-
RESIST COATINGS TO ATTACK BY HYDROFLUORIC ACID**

| Ultraviolet Exposure Time, Min. | Immersion Time in HF Etchant, Min. | Number of Pinholes | |
|---------------------------------|------------------------------------|--------------------|-------------------|
| | | Waycoat PF | Dynachem CMR-5000 |
| 1 | 5 | None | None |
| | 25 | None | None |
| | 45 | Numerous | Numerous |
| 5 | 5 | None | None |
| | 25 | Two | None |
| | 45 | Three | Twelve |
| 10 | 5 | None | None |
| | 25 | Five | One |
| | 45 | Twelve | Eight |

After the photoresist pattern was developed, oven baking was required to remove residual developer solvent prior to etching. Oven baking for 20 minutes at 185°F removed the same amount of residual solvent as oven baking for 10 minutes at 250°F. Oven baking for 10 minutes at 270°F embrittled the photoresist coating and made it less resistant to attack by hydrofluoric acid.

A uniformly clean substrate is required to obtain good adhesion of the photoresist coating to the substrate. Standard Grumman cleaning procedures have thus far proved to be most effective for aluminum substrates. Alkaline soak cleaning followed by flash etching in dilute hydrofluoric acid appears to be most promising for titanium substrates. The pretreatment processes studied initially are summarized in Table XVII.

TABLE XVII

EVALUATION OF PRETREATMENT PROCESSES

| Substrate | Pretreatment Process | Results |
|------------|--|--|
| Aluminum * | MEK Wipe Non-Etch Alkaline Soak Cleaner at 160°F Chromated Deoxidizer at 140-150°F | Excellent Adhesion Minimum Pinholing |
| Aluminum | MEK Wipe Non-Etch Alkaline Soak Cleaner at 160°F 15% Aqueous Phosphoric Acid Soak at 72°F | Excessive Pinholing |
| Aluminum | MEK Wipe Non-Etch Alkaline Soak Cleaner at 160°F | Poor Adhesion |
| Aluminum | MEK Wipe Alkaline Grit Scrub | Excessive Pinholing |
| Titanium * | MEK Wipe Alkaline Soak Cleaner at 160°F Chromated Conversion Coating | Excellent Adhesion Poor Pinhole Resistance |
| Titanium | MEK Wipe Alkaline Soak Cleaner at 160°F Flash Etch with Dilute HF | Excellent Adhesion Improved Pinhole Resistance |
| Titanium | MEK Wipe Alkaline Soak Cleaner at 160°F Flash Etch with Dilute HF 15% Caustic Soak at 230°F | Poor Adhesion |

* (Standard Grumman procedure)

None of these proved completely satisfactory. The data indicated that the following criteria must be met to reduce or eliminate poor photoresist adhesion and pinholing:

- Surface must be thoroughly clean
- Surface must be smooth
- A conversion coating or oxide must be uniformly applied

As a first approach, surface pretreatments were classified into the following four categories:

- Flash Etching
- Oxidation

- Conversion

- Flash Etching plus Conversion

The processing parameters for these pretreatment systems and their effect upon photoresist performance are summarized in Table XVIII.

TABLE XVIII

ADHESION AND ETCHANT RESISTANCE OF SURFACE-TREATED TITANIUM ALLOY TEST PANELS

| Surface Treatment | Solution Used | Immersion Time (Min) | Temp. °F | Photoresist Performance | |
|-------------------------|--------------------------|----------------------|----------|-------------------------|--------------------|
| | | | | Adhesion | Etchant Resistance |
| Flash Etching | 10%/vol HF | 0.25 | 72±2 | Good | Poor |
| | Nitric Acid Actane 70 | 1.00 | 72±2 | Good | Poor |
| Oxidation | 10%/wt NaOH | 10.00 | 175 | Poor | Poor |
| | 10%/wt NaOH | 10.00 | 225 | Good | Fair |
| | 50%/vol HNO ₃ | 10.00 | 225 | Good | Fair |
| | 50%/vol HNO ₃ | 15.00 | 240 | Good | Fair |
| Conversion | Pasa-Jell 107 | 5.00 | 72±2 | Good | Poor |
| Flash Etch + Conversion | 10%/vol HF | 0.25 | 72±2 | Fair | Poor |
| | Pasa-Jell 107 | 5.00 | 72±2 | | |
| | Nitric Acid Actane 70 | 1 | 72±2 | Poor | Fair |
| | Pasa-Jell 107 | 5 | 72±2 | | |

The most promising results were obtained with hot nitric acid pretreatment. Photoresist adhesion, however, was not completely uniform over the entire piece tested. In an effort to improve adhesion characteristics, all pretreatment methods that heretofore improved adhesion were combined into the following single pretreatment process:

- Wipe surface with methyl ethyl ketone to remove shop oils and dirt, and with Spray-White solution to remove stamping ink.

- Scrub surface with Shipley abrasive metal cleaner
- Immerse part in a non-etch alkaline cleaner solution at 160°F for ten minutes and then rinse in cold water for five minutes.
- Remove surface oxides by immersing part in nitric-octane solution for five minutes (a lustrous, smooth surface will be produced).
- Immerse part for 15 minutes in a boiling solution consisting of equal volumes of concentrated nitric acid (70 percent by weight) and water to produce a uniformly oxidized, light brown surface. Rinsing is not required after this step, because the hot acid solution evaporates rapidly from the substrate when it comes in contact with air at ambient temperature after the part has been removed from the processing tank.

Parts were coated with Waycoat PF photoresist immediately after pretreatment in one case and two days later in another. Printing and developing parameters were as follows:

- Photoresist viscosity at 72°F \pm 2°F - 50 seconds (Zahn No. 5 viscometer)
- Number of coats applied - three (from alternate edges of part)
- Curing Cycle - five minutes at 180°F after first coat, five minutes at 180°F after second coat, and 15 minutes at 250°F after third coat.
- Developing Cycle - 30-second immersion in Waycoat PF developer followed by 10-second spray with fresh developer and 10-second immersion in isopropanol.
- Post Curing - 15 minutes at 250°F

The imaged part was then immersed in a slowly agitated, 96°F-solution of ten percent by volume of hydrofluoric acid for one hour. No pinholes were observed in the coating after etching. The photoresist was then removed in Waycoat PF photoresist stripping solution.

The contoured photofabrication tooling was completed and evaluated (Figures 40 and 41). Excellent vacuum contact with the leading edge component and the test panels was obtained. The clear polyvinyl chloride membranes remained distortion-free after use, ultraviolet light transmittance was excellent, and the tooling materials did not deteriorate from handling or exposure to ultraviolet radiation.

6. AUTOMATIC SCRIBING OF MASKED PARTS

The scribing of parts in the chem-mill process for areas of mask removal is now a totally manual operation that requires tracing a template with a knife. Enough pressure must be applied to cut the mask without cutting into the part. The quality of the work depends wholly upon the skill of the personnel doing the scribing. This part of the work now represents 40 to 50 percent of the production costs of chem-milling a part.

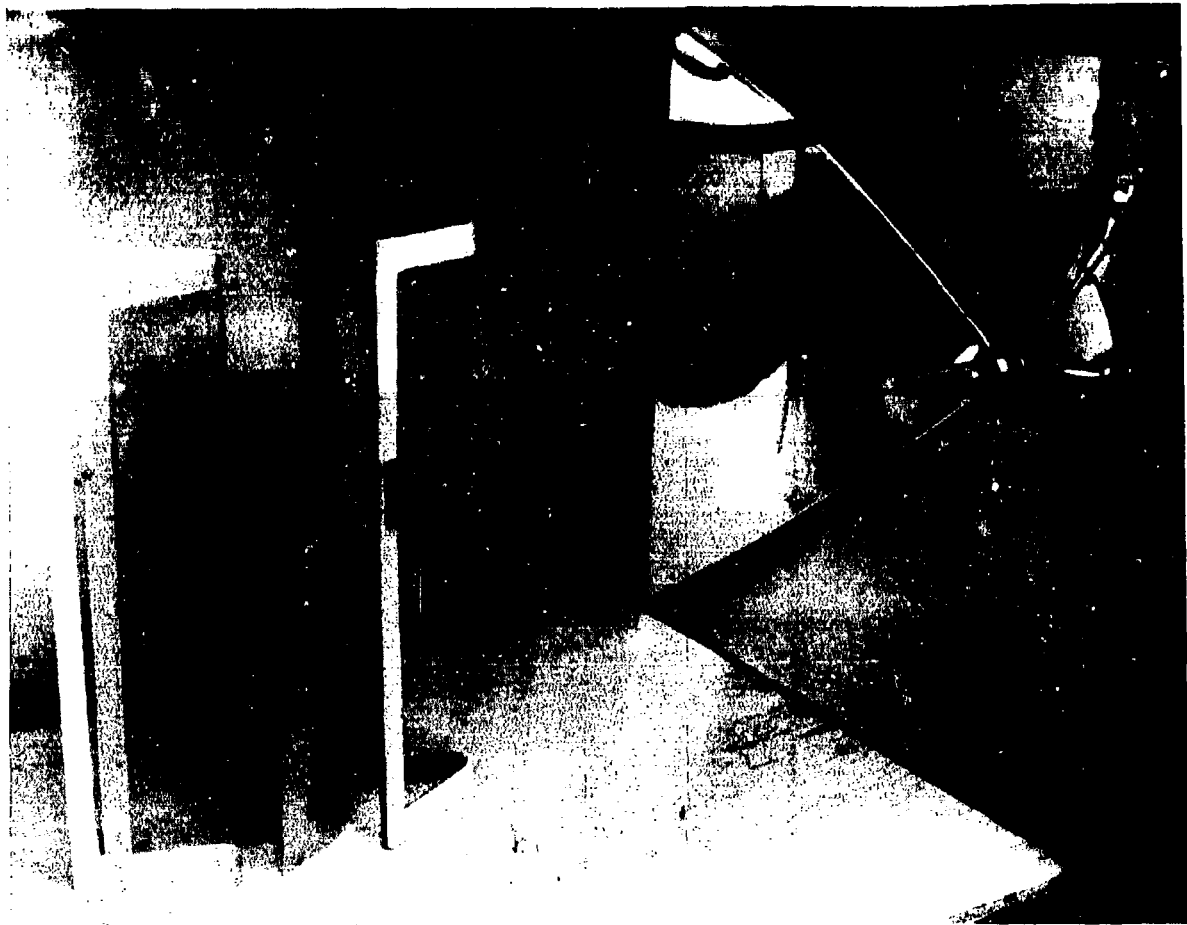


Figure 40 Formed Leading-Edge Part with Tooling and Ultraviolet Light Source

NOT REPRODUCIBLE

Figure 41 Formed Leading-Edge Part Inside Maskant Tool

The following methods of cutting maskants were evaluated:

- **Conventional Knife Cutting** - Tests were conducted to determine optimum knife materials, configurations and cutting forces. A knife holder was designed, fabricated, and installed on a Bridgeport milling machine (Figure 42). Cutting force requirements were determined by traversing a knife under a masked aluminum panel. All tests were conducted at a feed rate of 9 1/2 inches per minute. Thickness of the maskant varied between 0.007 and 0.013 inch. All knives were made of 1095 carbon steel.

Test results presented in Table XIV show that hand-scribing-type X-Acto knives will not be acceptable for automatic operations. When a constant force is applied to the knife, the depth of cut varies with the condition of the knife edge (See tests 7 and 8). Variation in maskant thickness caused scratch marks in the thin coated areas when a constant cutting force was applied. A more suitable knife material for automatic scribing would probably be tungsten-base high-speed steel. The problems of frequent sharpening would be eliminated with this material..

- **Water Jet Cutting** - Initial tests have demonstrated the ability of a high-velocity hydraulic jet to scribe masked parts. Using a 0.015-inch-diameter nozzle driven by a pressure of 3000 psi, chem-mill maskant was cut without affecting the base material. The jet used has a kerf of 0.007 inch. For chem-mill scribing, a finer kerf would be required.

Based on results of this investigation, a cutter head will be designed and built. The head will be installed on a machine capable of controlling cutter direction. The equipment was evaluated to establish potential cost savings and part quality compared to manual scribing techniques.

TABLE XIX

CUTTING FORCE DATA FOR SCRIBING KNIVES

| Test No. | Cutting Force (grams) | Angle of Knife with Respect to Work (degrees) | Number of Cuts on Blade | Remarks |
|----------|-----------------------|---|-------------------------|---|
| 1 | 300 | 30 | 0 | Knife cut partially through mask. Difficult to peel off |
| 2 | 360 | 30 | 1 | Knife cut through mask without affecting Al plate |
| 3 | 400 | 30 | 2 | Knife cut through mask without affecting Al plate |
| 4 | 450 | 30 | 3 | Slight marking of Al plate |
| 5 | 500 | 30 | 4 | Slight marking of Al plate |

TABLE XIX (Continued)

| Test No. | Cutting Force (grams) | Angle of Knife with Respect to Work (degrees) | Number of Cuts on Blade | Remarks |
|-------------------------|-----------------------|---|-------------------------|---|
| 6 | 550 | 30 | 5 | A well-defined scratch two inches long |
| 7 | 550 | 30 | 6 | A well-defined scratch two inches long |
| 8 | 550 | 30 | 10 | Knife cut through mask without affecting Al plate |
| BLADE BEGINNING TO DULL | | | | |
| 9 | 150 | 70 | 0 | Good cut; no affect on Al plate |
| 10 | 200 | 70 | 1 | Good cut; no affect on Al plate |
| 11 | 250 | 70 | 2 | Knife cut through mask; slight scratch on plate |
| 12 | 250 | 70 | 3 | Knife cut through mask; slight scratch on plate |
| 13 | 250 | 70 | 8 | Good cut; no affect on Al plate |
| 14 | 250 | 70 | 0 | Knife cut through mask; slight scratch on plate |

A step toward automating the scribing of masked parts is to utilize photo-electric line-following techniques or numerical control systems for more difficult workpieces. A Grumman-built X-Y plotter (Figure 43) was used to automatically scribe flat parts. The potential advantages of this system are reduced manual work, consistent quality of workmanship, and lower tooling costs. These advantages are particularly important in the case of large titanium skins which are difficult to scribe manually and which are sensitive to scratching.

The wall-mounted X-Y plotter was used as a test fixture to hold a water-jet cutting nozzle. The X-Y plotter was also adapted to hold a conventional knife for maskant scribing. The table of the X-Y plotter can handle panels up to 60 by 72 inches. Drives were installed to give the table a speed capability of 200 inches per minute. The best drives consist of low-inertia, DC servo-motors driven by solid-state servo-amplifiers that give a torque output of 140 ounce-inches. The present system is driven by electrical stepper motors which are undesirable because of the pulsating motion generated, even though

NOT REPRODUCIBLE

Figure 10 Scribing Knife in Holding Fixture

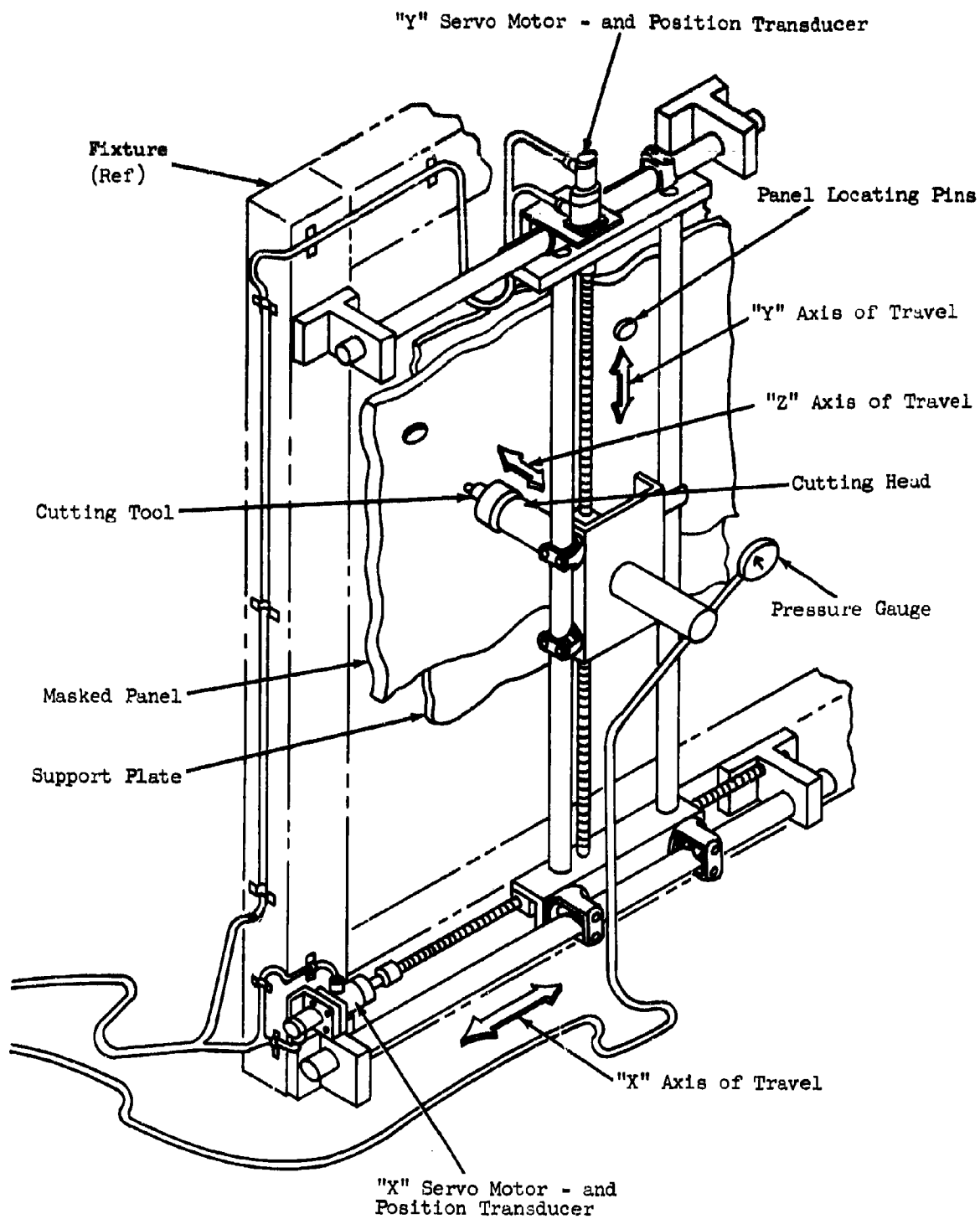


Figure 43 X - Y Plotter Schematic

torque output is sufficient.

Initial tests conducted at the R. Dudgeon Company, New York, New York, showed the feasibility of using a high-energy hydraulic jet to scribe masked parts. A high-pressure water system was used to drive an 0.008-inch-diameter cutting nozzle. Tests were conducted previously at Grumman using oil as the cutting fluid. Since water is more dense than oil, less mist was produced. The use of water also eliminates cleaning of the panels after scribing and possible maskant attack by the oil. A water system was purchased from the R. Dudgeon Company and installed on the Grumman X-Y plotter.

The high-pressure water system (Figure 44) consists of a pneumatically driven, reciprocating piston pump with a maximum output capacity of 100 cubic inches per minute at a pressure of 6000 pounds per square inch. A nitrogen-charged piston accumulator, tied into the output port of the pump, is used to dampen pressure pulsations. The unit is also equipped with an air filter, regulator, and lubricator. A 10-micron water filter was installed on the output side of the pump to eliminate possible blockage of the small-diameter nozzles.

A nozzle cutting head was designed, fabricated, and installed on the plotter carriage (Figure 45). The head consists of a nozzle holder attached to an adjusting screw which controls the nozzle position in the Z axis. The cutting head is mounted on a trunnion that can be rotated to determine the most efficient jet cutting angle.

Initial water cutting tests were performed on parts coated with Turco 522 maskant using an 0.008-inch-diameter rounded approach nozzle at a feed rate of 50 inches per minute and a pressure range of 2000 to 3000 pounds per square inch. The high-velocity jet had no adverse effect on the base material. Cutting tests were also conducted on neoprene-masked parts (Figure 46).

Most chemical milling operations being carried out today involve pre-scribing of all etch lines. Since kerf widths in excess of 0.005 inch could affect application of the prescribing sealant, several rounded-approach and sharp edged orifices of various diameters were evaluated in an attempt to reduce kerf width. The smallest diameter nozzle commercially available was an 0.008-inch-diameter, rounded-approach nozzle made by the Water Cooling Corporation of Rosedale, New York. A sharp-edged orifice was made with an 0.0059-inch-diameter drill to reduce the water exit stream diameter. An initial test of this orifice showed that it contracted the exit stream and then diverged it. Using this nozzle produced non-uniform cuts, since varying nozzle-to-part distances were produced by flatness runout in the masked panel. In an attempt to produce smaller diameter orifices, 0.0019 and 0.0031-inch-diameter cobalt spiral pilot drills were purchased from the Fineisen Company of Westwood, New Jersey. Nozzles of different forms and varying orifice diameters were tested over a wide range of cutting speeds and angles. Two of these nozzles are shown in Figure 47. Since it has been shown that the maskant cut-through line should be as fine as possible to prevent lifting and facilitate resealing of scribed lines for successive peeling in step-etching operations, nozzles with finer openings were made. One fabrication method involved initial swaging of 0.250-inch-outside-diameter/0.049-inch-thick-wall stainless

NOT REPRODUCIBLE

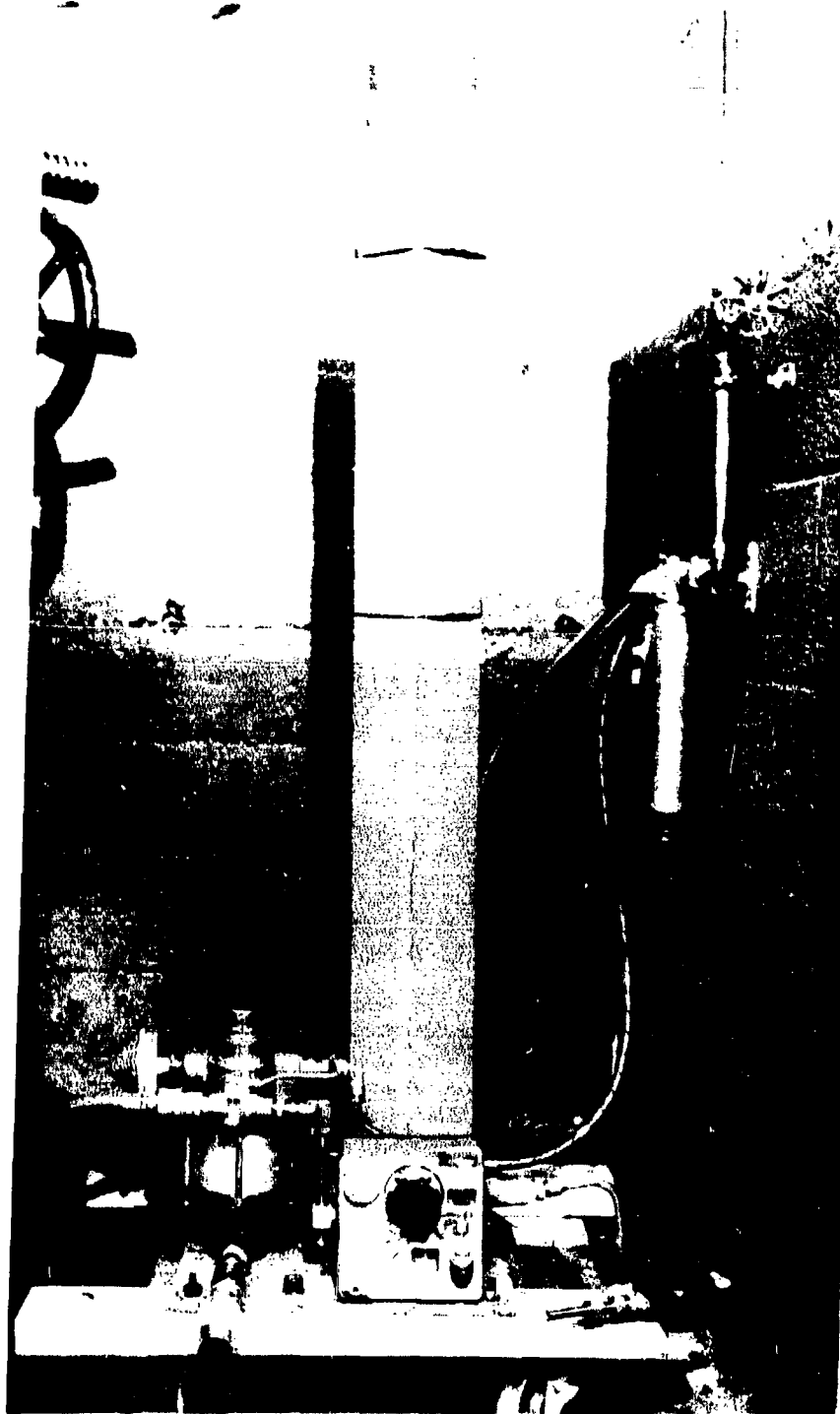


Figure 44 High-Pressure Water System

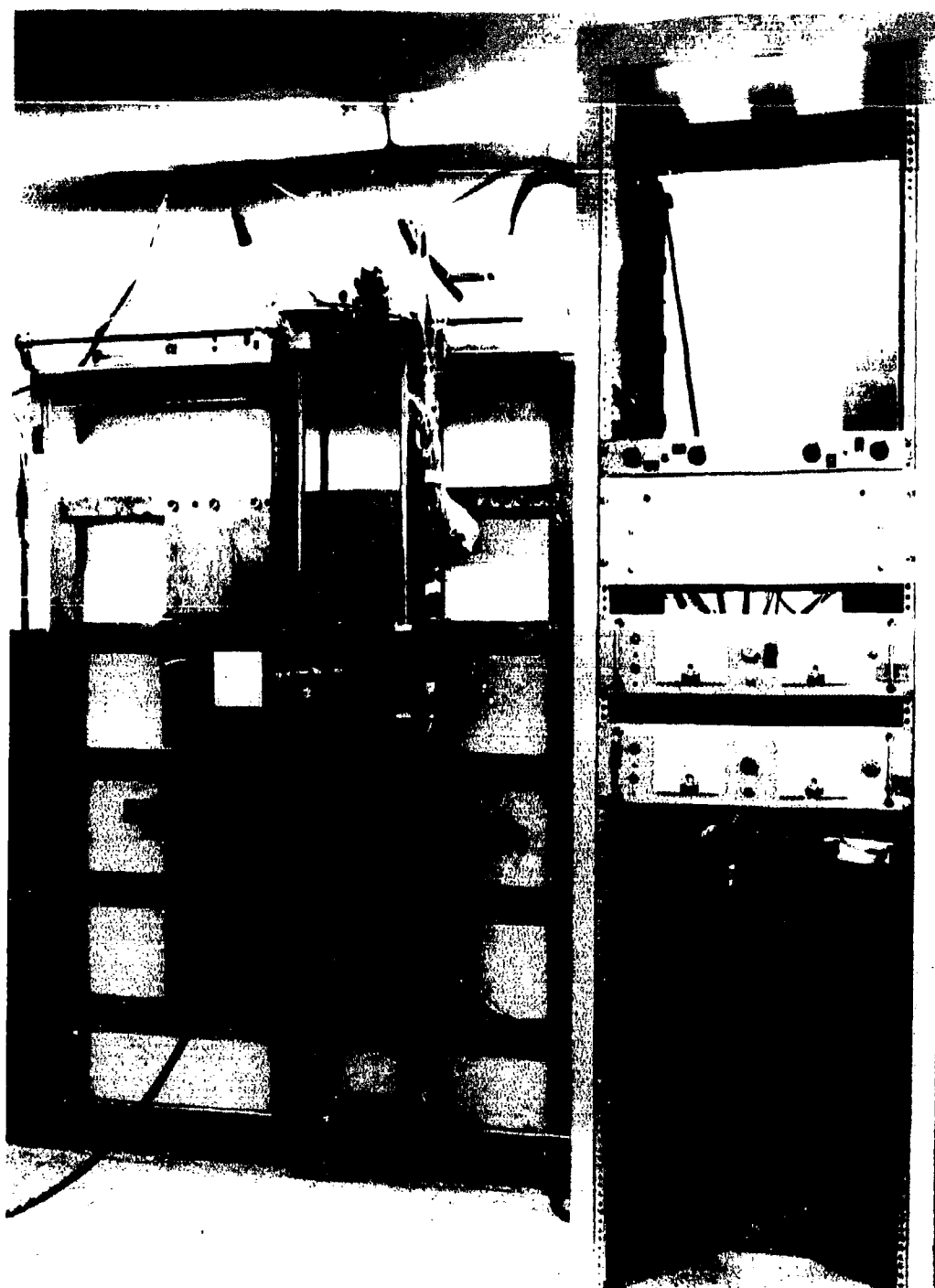


Figure 45 X-Y Plotter with Water-Jet Cutting Head

NOT REPRODUCIBLE

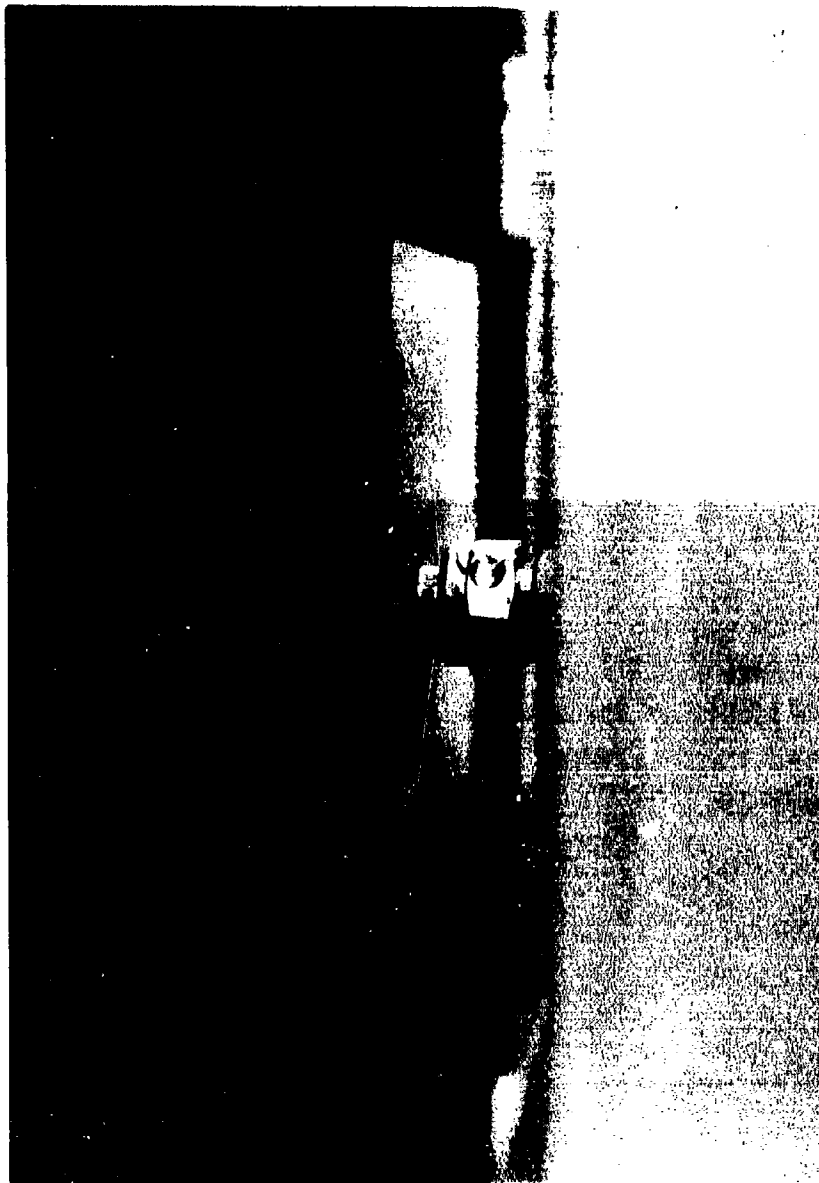


Figure 46 High-Pressure Water-Jet Cutting of Neoprene-Masked Panel

TABLE XX

Summary of Water-Jet Maskant Scribing Tests

| Type of Nozzle | Pump Air Pressure, psi | Head Space, inch | Travel Rate, inches per min. | Nozzle Pressure, psi | Remarks |
|-----------------|------------------------|------------------|------------------------------|----------------------|---------------------------------|
| Machine Drilled | 80 | .010 | 120 | 4500 | Did not cut thru; ragged |
| | 80 | .010 | 90 | 4500 | Partial cut thru ; ragged |
| | 85 | .010 | 120 | 4000 | Did not cut thru; ragged |
| | 85 | .010 | 60 | 4000 | Best cut, but not clean |
| | 88 | .010 | 90 | 4000 | Did not cut thru; ragged |
| | 88 | .010 | 90 | 4500 | Partial Cut thru; uneven edges. |
| Laser Drilled | 95 | .090 | 20 | 5500 | 90% cut thru; some lifting |
| | 95 | .090 | 20 | 5500 | 90% cut thru; some lifting |
| | 95 | .090 | 20 | 5500 | 90% cut thru; some lifting |
| | 100 | .090 | 20 | 6000 | 95% cut thru; little lifting |
| | 100 | .090 | 20 | 6100 | 95% cut thru; less lifting |
| | 100 | .090 | 20 | 6100 | 95% cut thru; less lifting |
| | 100 | .090 | 10 | 6400 | 97% cut thru; no lifting |

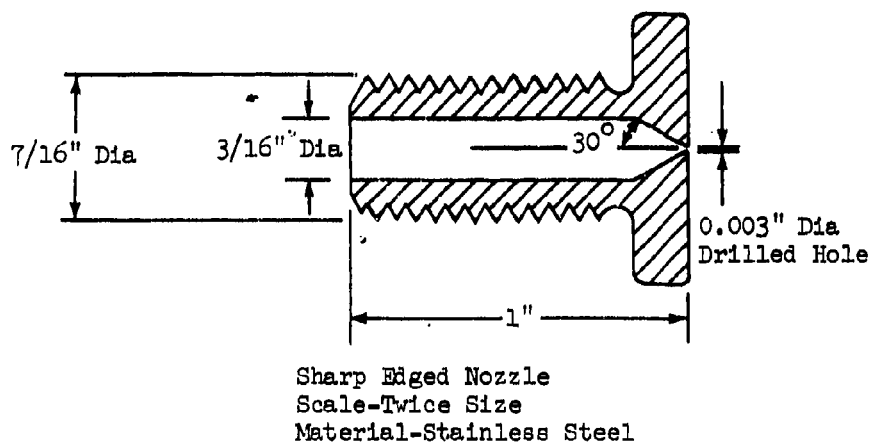
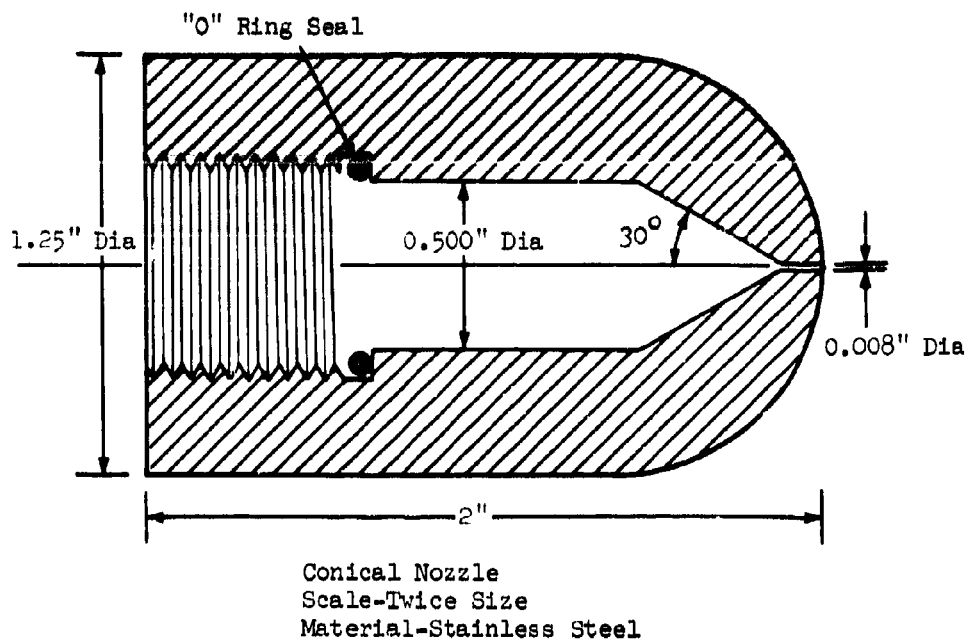


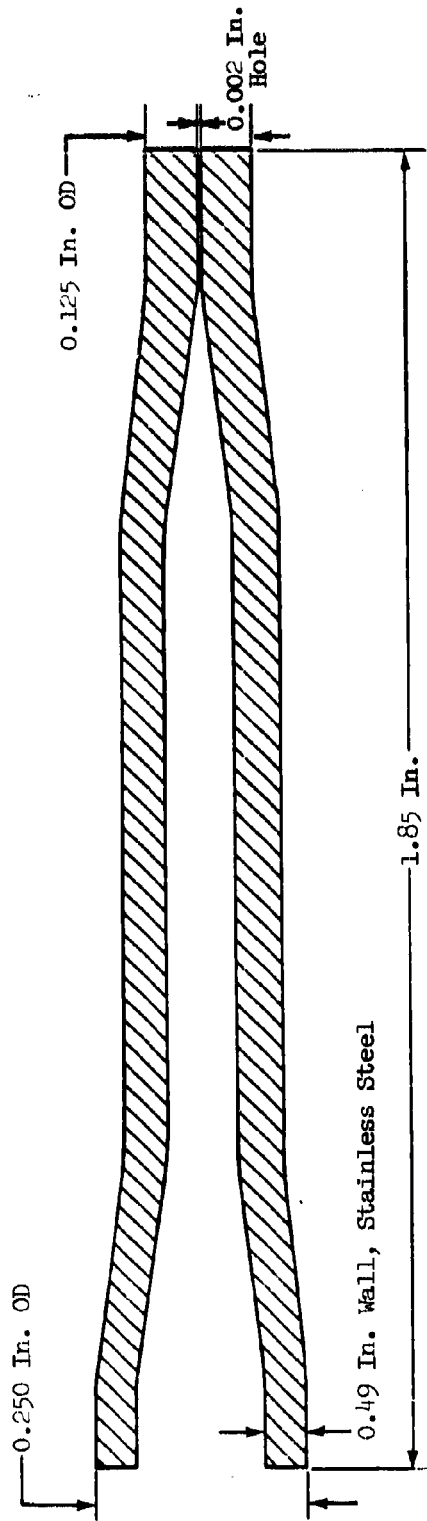
Figure 47 Experimental Nozzles Used in High-Energy Water.
Jet Scribing of Chem-Mill Maskants

steel tubing to an outside diameter of 0.1875 inch. A second swaging operation further reduced the outside diameter to 0.125 inch and the inside diameter to 0.002 inch (Figure 48). The orifice diameter can be enlarged by grinding off the face of the opening to that portion of the internal taper desired. An automatic shutoff valve was installed in the automatic scribing system to prevent lifting of the maskant when the scriber stops.

The ideal scribed line on masked metal parts that are to be etched in hydrofluoric acid solutions should be about 0.005 inch wide, have smooth edges and penetrate to about 95 percent of the maskant thickness. The remaining five percent of the maskant in the scribed line should break off easily when the unwanted portion of the maskant is peeled off without causing the edges of the maskant that should remain on the part to lift off. If the scribing tool should penetrate all the way through the maskant to the metal surface, the scribed lines would have to be resealed in those sections that are to be subjected to progressive chemical milling operations.

A mechanical scribing method that offers promise for automation is hydraulic jet cutting with a fine jet of water under high pressure. With hydraulic jet scribing scratch damage is eliminated, since the degree of water pressure used can only groove the maskant. In addition, even large variations in pressure will not damage the metal part. The hydro-jet cutting process is being used to trim flash from fiberglass moldings and to cut cloth, plywood, and rubber stock. In some cases, the jet is moved over the work while in others the work is moved under a fixed jet (usually when very high pressures are used).

Equipment used in the establishment of the hydro-jet masking cutting process consisted of a high-pressure water pump, an accumulator to store the high-pressure water and to smooth out pump surges, a fine nozzle to direct the jet, automatically controlled valves to activate and de-activate the jet, and apparatus to move either the jet or the workpiece to give the desired scribe-line configuration. The piston-type accumulator should be fabricated from non-corrosive metals to prevent the formulation of rust particles that could clog the fine nozzle opening. Traversing of the mechanism, starting of the pump (after the initial pressure build-up), and opening of the valve to allow water to flow to the nozzle should all occur simultaneously. If the jet is allowed to operate in one place for an extended period of time, the water flow will eventually lift the maskant from the metal surface in that area. The accumulator should be proof-tested to 150 percent of the highest operating pressure. Development work in the high-pressure range was limited by the pressure capacity of the piston-type accumulator that was used.



Swaged Nozzle (5 Times Actual Size)

Figure 48 High-Energy Water-Jet Maskant Scribing Nozzle
Fabricated by Two-Step Swaging Operation

The traversing mechanism should be capable of maintaining a uniform rate of travel to prevent the formation of jagged-edged grooves in the maskant. The mechanism should be set up so that there is no drag from the hydraulic lines or electrical wiring as the nozzle carriage traverses across the workpiece. Some degree of adjustment in the rate of travel is necessary, since the extent of penetration of the water jet through the maskant is directly proportional to the dwell time of the jet over an area. Vibration of the drive mechanism should be minimized to obtain smooth travel of the jet carriage, which, in turn, will give a smooth maskant cut.

Rapid-response, rotary, solenoid-actuated valves work best in hydro-jet masking scribing equipment. Repeated opening and closing of the stem-and-seat type valves under high pressure usually results in leakage and lack of accumulation pressure. In the laboratory equipment used, the air supply valve to the pressure pump is activated by a solenoid from the same actuating circuit that opens the nozzle pressure valve.

A Bendix Model MS 28720-12 filter with Element No. AN 6235-4A was used to remove the dirt particles from the water to prevent clogging of the nozzle. At pressures above 5200 psi the aluminum housing tended to distort. Some leakage occurred, until larger O-rings were installed in the connections.

The following types of nozzles were evaluated:

- Flat, stainless steel, insert discs with small-diameter drilled holes
- Machined nozzle with conical and sharp-edged drilled orifices
- Stainless steel swaged tubing
- Insert discs with laser-beam drilled holes

The flat, stainless steel, insert disc and machined nozzles did not produce a satisfactory water jet because the diameter of the drilled holes was larger than that of the drill (0.006-0.0008 versus 0.003 inch). The 0.032-inch-thick stainless steel insert discs bulged after repeated use at the high pressures (5000 psi and above) needed to provide satisfactory grooves in the maskant. The insert discs should be at least 0.060 inch thick. The high drill breakage rate made these nozzle fabrication methods impractical. The average tube nozzles were also unsatisfactory because of internal longitudinal grooving and ragged openings. It was also difficult to control hole size. Tubes swaged under identical conditions had different sized openings at the reduced ends.

Laser drilling equipment has been refined to the extent that many materials can now be drilled with the laser beam. The Raytheon Corporation of Waltham, Massachusetts, was queried on drilling small-diameter holes in stainless steel discs. Using a YAG, solid-state pulsed laser, Raytheon personnel were able to drill small-diameter holes in 0.032-inch-thick stainless steel discs with one pulse per hole. The smallest holes ranged in diameter from 0.0020 to 0.0032 inch, while the largest holes ranged in diameter from 0.006 to 0.007 inch. A typical laser-drilled hole in 0.032-inch-thick stainless steel sheet is shown in Figure 49. Holes can also be laser-drilled in diamonds. A diamond nozzle would last considerably longer than a stainless steel nozzle. It is estimated that the holes in stainless steel nozzles would be worn to too large a diameter after being used in production about one week.

Maskant scribing tests were conducted with the machined and laser-drilled nozzles. Maskant scribing cuts made with a laser drilled nozzle are shown in Figure 51. Data obtained are presented in Table XX. The results indicate that high-pressure water gives a more uniform cut. Although pressure as high as 10,000 psi could not be tried because of equipment strength limitations, extrapolation of the data indicates that a water pressure of 10,000 psi would give the highest quality scribed line. The smallest nozzle diameter that could be practically used at the maximum available pressure of 6400 psi was 0.003 inch. The water jet produced by the 0.002-inch-diameter nozzle at 6400 psi diverged considerably. It is possible that the 0.002-inch-diameter nozzle could be used effectively at water pressures higher than 6400 psi. Nozzle inserts were tested with the smallest and the largest parts of the holes as the exit. Better cuts were obtained using the nozzle insert with the narrowest part of the hole as the exit.

At a given pressure, the travel rate must be reduced as the size of the water jet is decreased (see Table XX). For example, with an 0.008-inch-diameter nozzle, a travel rate of 60 inches per minute must be used; with an 0.003-inch-diameter nozzle the travel rate must be reduced to 20 inches per minute.

It was also found that if the nozzle is too close to the maskant surface, bounce-back of the water spray interferes with the cutting action of the water jet giving a ragged cut. Movement of the nozzle can also be stopped by high surface irregularities of the maskant. Optimum head space is about 0.090 inch.

High-speed films were taken of the cutting action of the water jet to study jet formation and maskant cutting effectiveness (Figure 50). Considerable difficulty was encountered in removing the glare caused by flood lights shining on the maskant. The close proximity of the nozzle to the surface being cut resulted in the generation of a considerable amount of spray that degraded the nozzle stream definition. The manner in which the traversing equipment was constructed made it impossible to place the camera at the best angle for photographing the scribing action. Definitive conclusions could not be drawn from analysis of the high-speed films because the water spray blurred the cutting action occurring at the maskant surface.

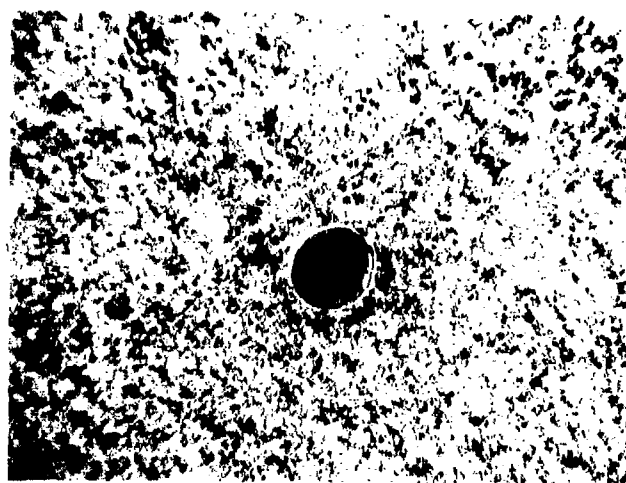


Figure 49 Laser-Drilled Hole in 0.032-Inch-Thick Stainless Steel
(500x Magnification)

NOT REPRODUCIBLE

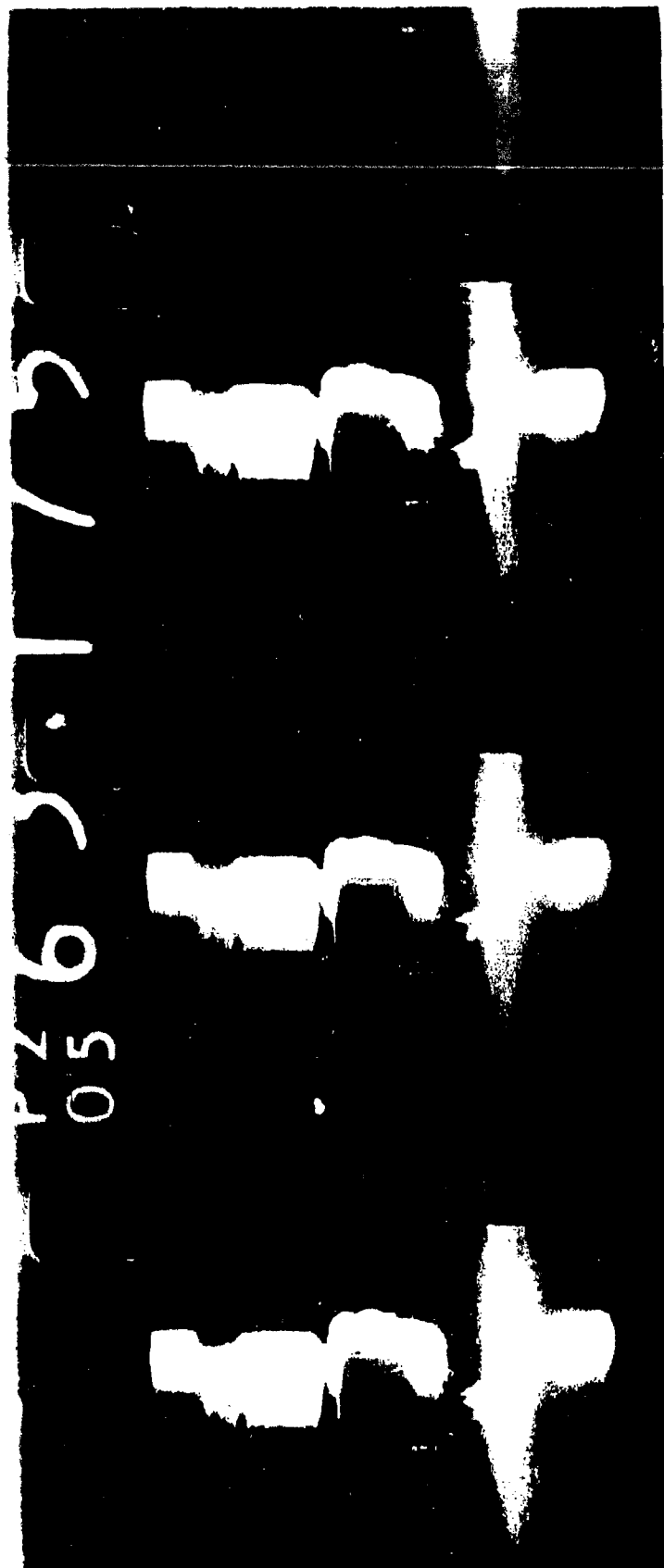
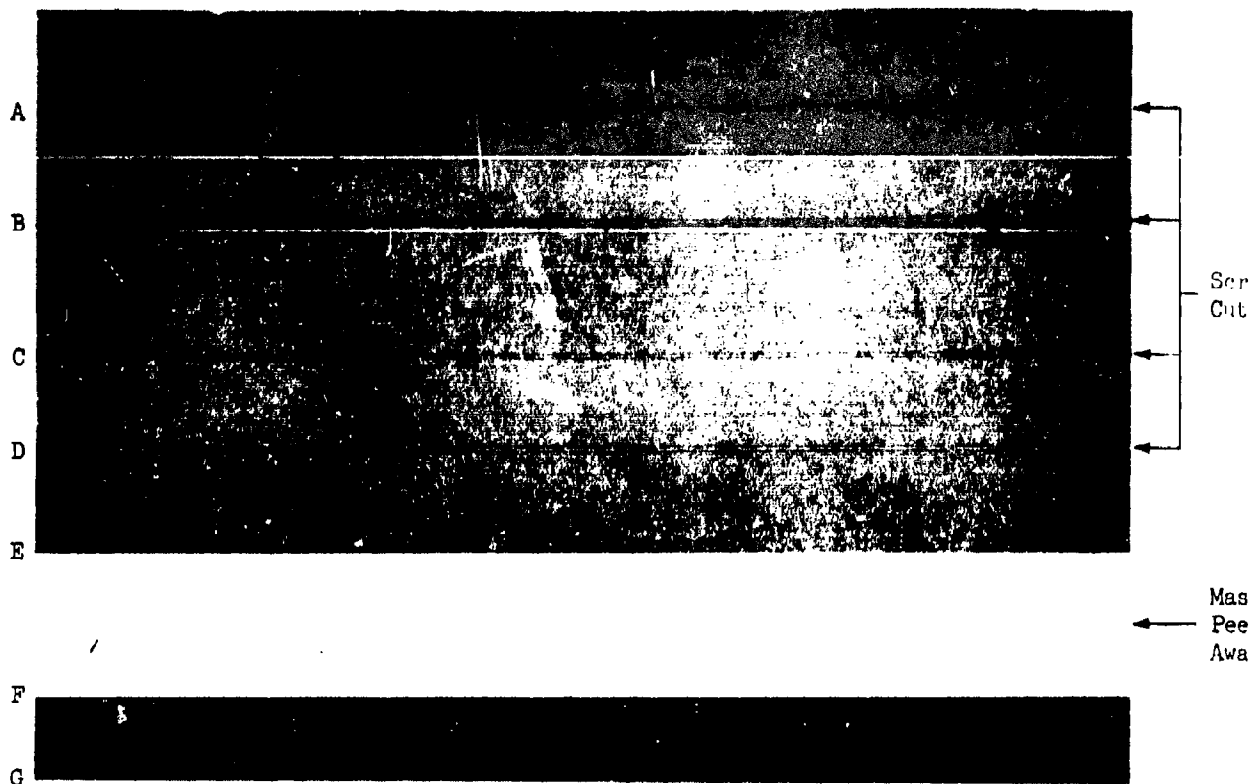


Figure 50 Frames of High-Speed Film of Water-Jet Cutting



a. Scribing Cuts and Peeled Strip (1x Magnification)

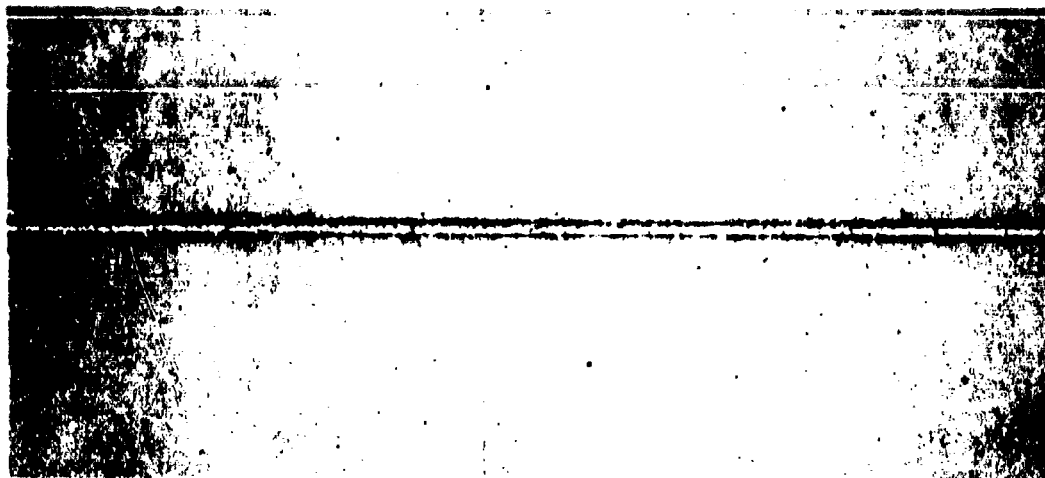


b. Peeled Strip Showing Smooth Sides of Peeled Area with
.. Little Lifting of Maskant (3x Magnification)

A

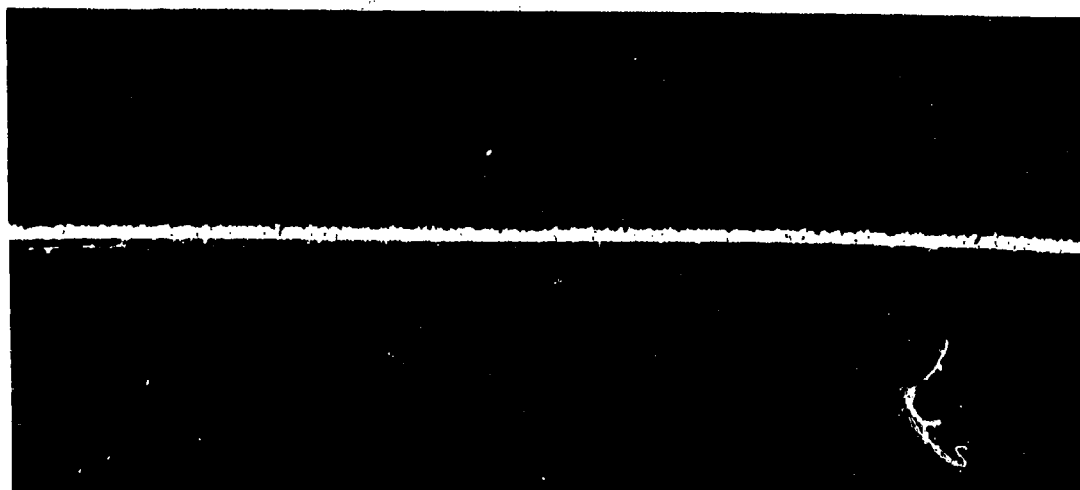
scribing
cuts

maskant
peeled
away



c. Scribing Cut "D" (5x Magnification)

NOT REPRODUCIBLE



d. Cross-Section of Scribing Cut "D" (5x Magnification)

Figure 51 Maskant Scribing Cuts Made
with 0.003-Inch-Diameter
Laser-Drilled Nozzle

113/114

B

To optimize quality of the scribed cut in the maskant, it is recommended that the nozzle insert be thicker to give a longer tapered hole to further increase water velocity and that the sides be polished. This can be obtained by using a diamond nozzle such as the type used in wire drawing. Cost of such a diamond nozzle would be less than \$200. Water pressure should be raised to 10,000 psi so that the travel rate can be increased. This will produce the desired fine, smooth depth of cut. The entire maskant scribing system could be programmed to cut continuously in closed lines, thereby eliminating the time-consuming, manual scribing work that is currently necessary. It is also recommended that a "feeler foot" precede the nozzle and be used to keep the nozzle at a constant distance from the maskant surface, thereby giving a more uniform cut. Proper application of the water jet cutting system could result in large savings in manpower while increasing production rates.

7. MASKANT PINHOLE DETECTION TECHNIQUES

Currently used maskants for chem-milling must be checked visually for small pinholes that are generally caused by air bubbles in the mask or by handling damage. In either case, the holes must be found and patched prior to chem-milling, or the part must be scrapped. The following methods were investigated to check parts for pinholes:

- Spark Testing Method. A porosity detector (Type 500/10k. SB/2) was purchased from the Allen P. Webb Company, 24 Stone Street, New York, New York. This equipment gives a visual observation of electric arcing through pinholes to a grounded part (Figure 52). Initial tests performed on Turco 522 masked (styrene-butadiene) parts gave excellent results. Pinholes which were not visually evident were easily detected using the spark tester. Arcing for extended periods of time showed no discoloration of the part or evidence of dielectric puncture even in thinly coated areas. Tests conducted on Organoceram 1010 neoprene mask were not satisfactory. Because of the material's low electrical resistance at high voltages, no differentiation between pinholes could be detected. The unit failed to register any difference between a bare aluminum surface and the neoprene-coated surface.
- Voltage Gradient Around Pinhole Method. Figure 53 shows a system that incorporates a sweep of the part with a wet sponge probe connected to an oscillator. A dc potential of 25 volts is placed on the part through a wire taped to the part prior to application of the mask. The wet sponge or perhaps a roller is swept across the surface of the part in all areas to be checked. When the sponge passes over an area containing a pinhole, conductivity through the wet sponge and into the wand causes an abrupt increase in the oscillator frequency (Figure 54). Experiments with this wet probe have shown good response when approaching the initial pinhole. As the part is wetted by the electrolyte used in the sponge, subsequent holes are undetectable because conductivity takes place through the electrolyte to the preceding hole. The voltage-gradient method worked well with styrene-butadiene maskant. A discernable change in output was not observed, however, when the wand was placed over a pinhole in a neoprene-masked panel. This occurred because the resistance

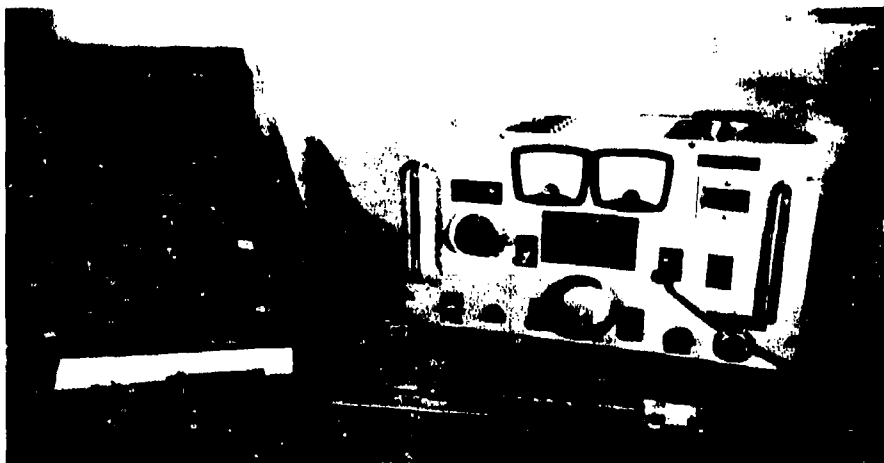


Figure 52 Spark Tester

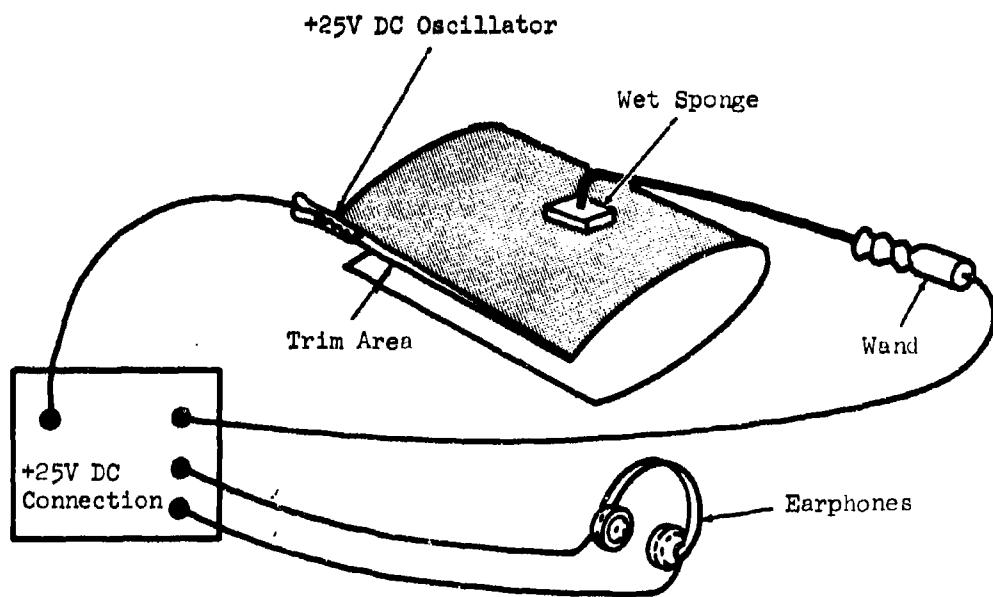


Figure 53 Pinhole Detection-Voltage Gradient Method-Wet Sponge Probe

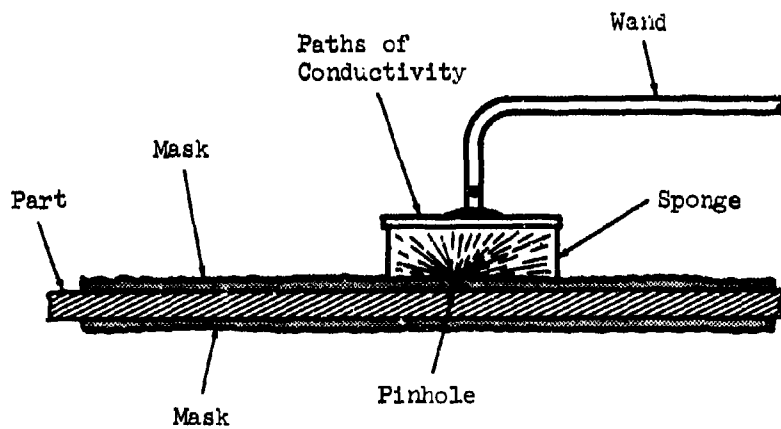


Figure 54 Pinhole Detection - Paths of Conductivity from Pinhole to Wand

of the neoprene maskant was equivalent to that for the sponge.

The apparatus shown in Figure 55 was used to check the resistance of neoprene and styrene-butadiene maskants. A sheet of test material of known thickness was placed between and in contact with two conductive aluminum blocks. The contact surface area was measured. Clamping force was held constant. After a variable voltage was impressed across the blocks, current flow was monitored with a galvanometer. Current-voltage relationships were obtained for neoprene sheet (Figure 56). Curves could not be obtained for styrene-butadiene because conductance was so low that current flow could not be detected with a 75-0-75 microampere galvanometer. Tests were run with the neoprene sheet dry and with the neoprene sheet moistened on one side with Oakite 164 electrolyte. Voltage was varied between zero and 50 volts DC. A test conducted at 110-volts DC showed that the neoprene sheet had a resistivity of 3.5×10^{10} ohms-mil²/foot which is too low for detection with a spark tester.

Another technique investigated involved submerging the part in a conductive medium (Figure 57). A wand was used to detect a pinhole in the mask. If there is a hole, conductivity takes place between the part at the hole and the wand through the water medium. The further away the wand, the greater is the water resistance and less is the effect on the oscillator.

- **Fluorescent Dye to Detect Pinholes.** Several dye materials were evaluated for their effectiveness in detecting pinholes in chem-mill maskants. Although not all dye materials fluoresce, the non-fluorescent types have exceptional brilliance in ordinary light.

Dye materials evaluated included the following:

| <u>TRADE NAME</u> | <u>MANUFACTURER</u> |
|------------------------------------|---------------------|
| Calcofluor White RWP | American Cyanamid |
| Pyla-Cert D.C. Yellow #7 | Pylam Products |
| Pyla-Krome Oil Fluorescent LX-5880 | Pylam Products |
| Pyla-Flor White S-5 | Pylam Products |
| Methyl Violet 2B Base | Allied Chemical |
| Plasto Yellow Y | Allied Chemical |
| Rhodanine B 500% | Allied Chemical |
| Uramine Concentrate | Allied Chemical |

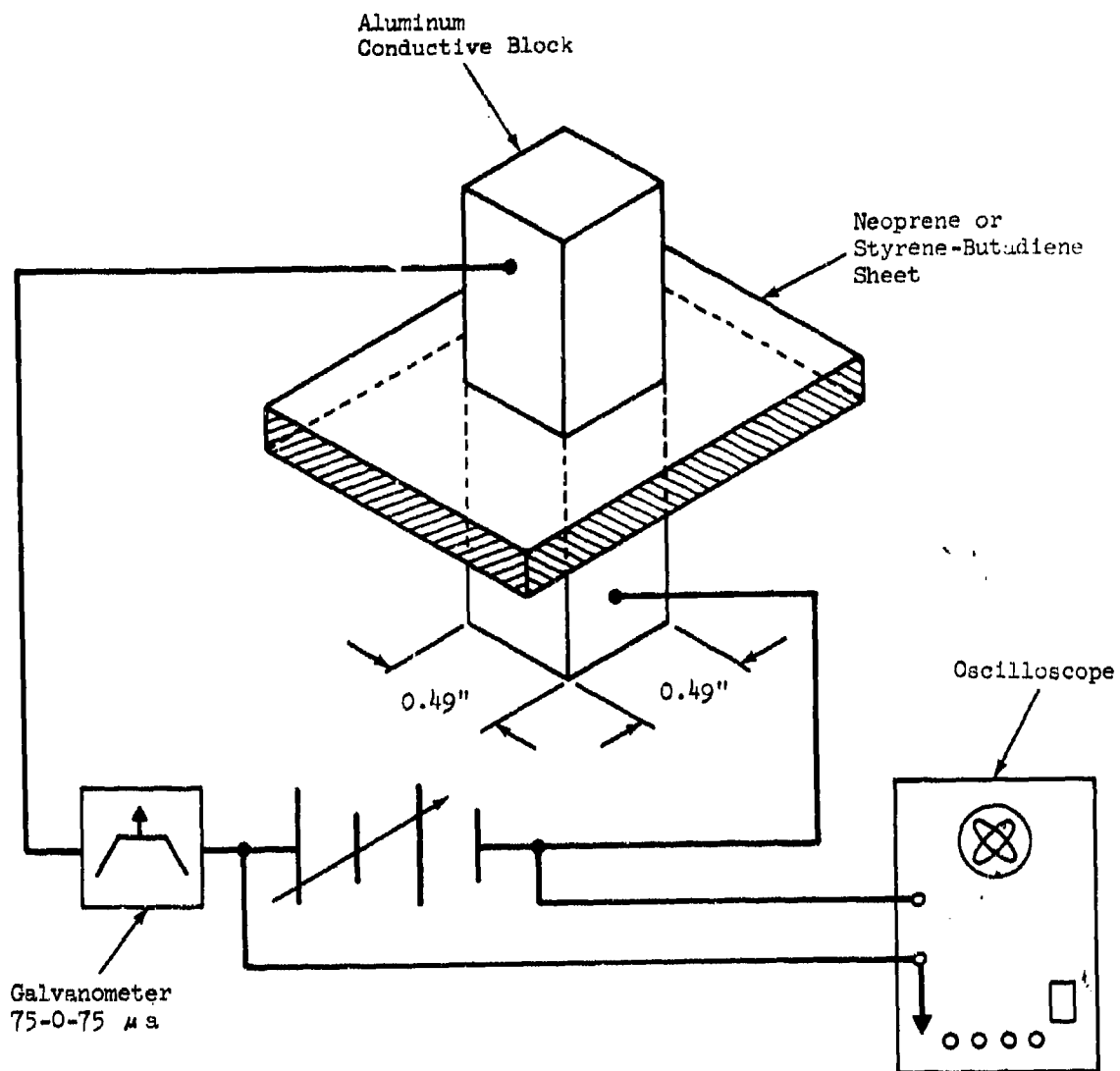


Figure 55 Test Arrangement for Measuring Conductivity of Neoprene Maskant

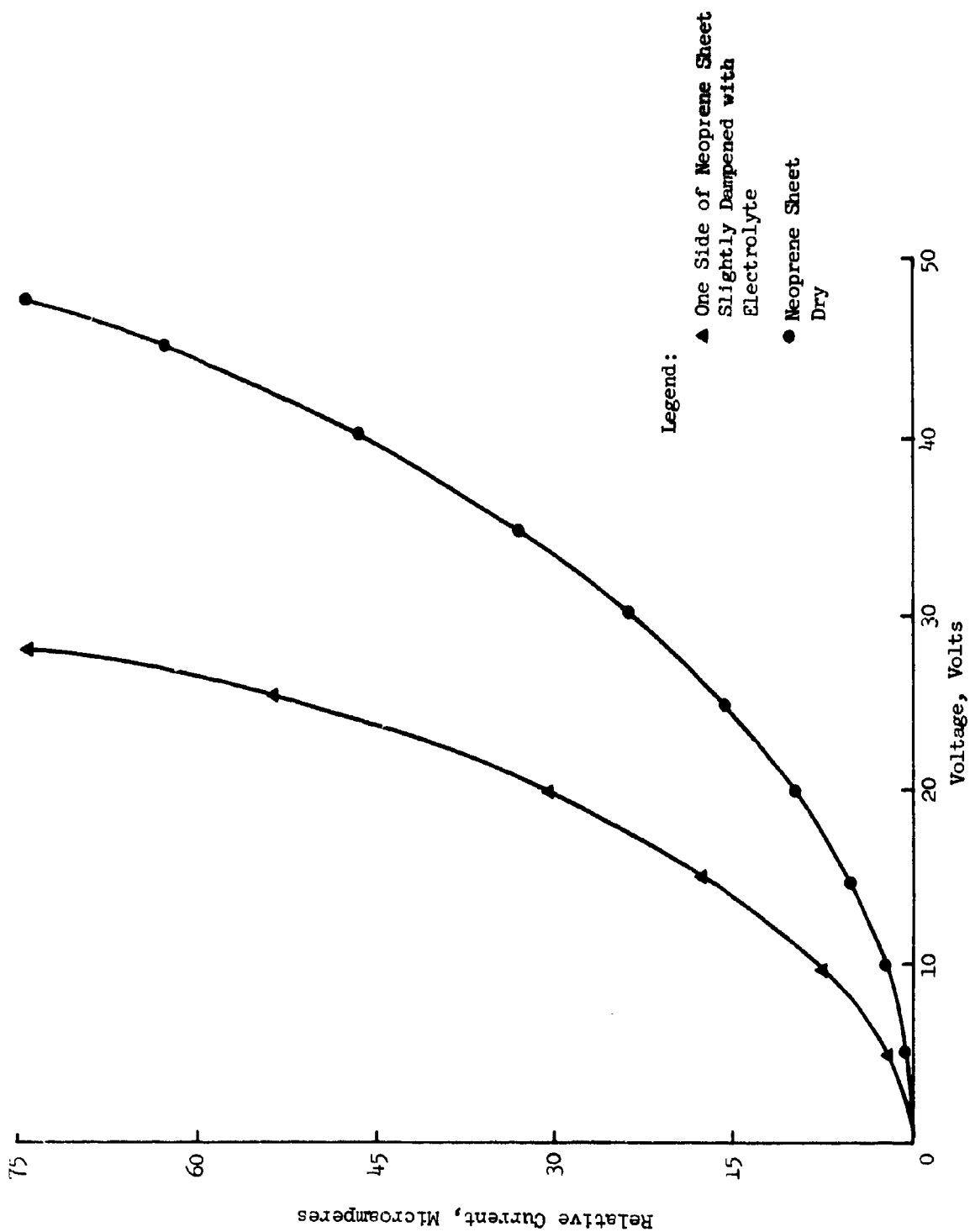


Figure 56 Conductivity of 0.49 x 0.49 x 0.011-inch Neoprene Sheet

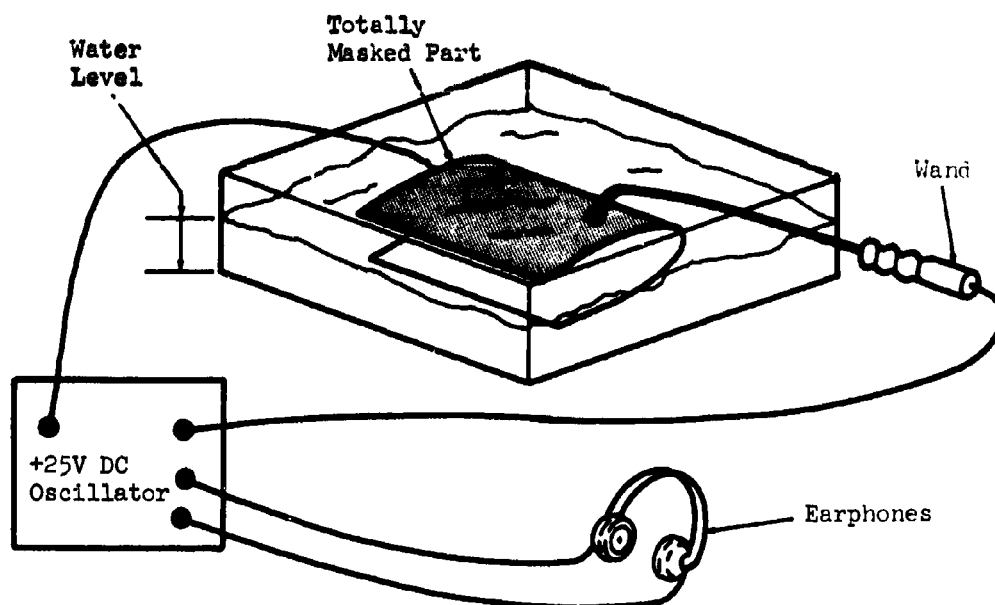


Figure 57 Pinhole Detection-Voltage Gradient Method-Wand Detector

The following techniques for using fluorescent dyes to detect pinholes in neoprene maskant were evaluated:

- Application of dye to uncoated aluminum by immersion in solvent solution of the dye prior to masking.
- Incorporation of dye in the maskant system prior to applying maskant to bare aluminum.
- Application of dye to the masked aluminum by immersion in a solution of the dye.

Tests were conducted to determine if the dye would fluoresce selectively from the aluminum surface at breaks in the maskant when exposed to ultra-violet light. The only promising material was Pylafluor White S-5. When neoprene-coated aluminum was immersed in an alcohol solution of the dye for ten minutes, a high-intensity fluorescence was observed on the bare aluminum at pinholes and at other breaks in the maskant, while no fluorescence was observed on the neoprene surface. During solvent evaporation, dye particles accumulated along the edges of the masked panel in sufficient quantity to fluoresce. This interfered with accurate detection of pinholes on edges and corners. Test results are summarized in Table XXI.

TABLE XXI
SUMMARY OF FLUORESCENT DYE TESTS

| Application Method | Fluorescent Dye | Concentration | Coating Characteristics | Fluorescence |
|--|------------------------|---|---|--|
| Immersion of aluminum panel in dye solution prior to masking | Rhodamine B Conc. 500% | 0.2-0.4% in equal volumes of methanol and water | Poor; dye particles did not adhere to panel uniformly | None |
| | | 1000 ml of above soln plus 80 grams of Atlas G695 as thickening agent | Poor; non-uniform | None |
| | | 50 ml of above solution was added to 160 grams of Aircoflex as thickening agent | Fair; not completely break-free | None |
| | | 1% in equal volumes of methanol and water | Poor | None |
| | | 1% in equal volumes of methanol and water on Alodine-treated aluminum | Good | None |
| | Calcofluor RWP | 1% in Xylene | Good | None |
| | Pyla-Cert D/C Yellow | 0.25% in methanol | Good | None |
| | Pylafluor White S-5 | 0.33% in methanol | Good | Fluoresced strongly on bare panel; -did not fluoresce through masking pinholes |

TABLE XXI (Continued)

| Application Method | Fluorescent Dye | Concentration | Coating Characteristics | Fluorescence |
|--|--------------------------------|--|-------------------------|---------------------------------------|
| Incorporation of dye in maskant prior to application to part | Check-Bond Phosphor Dispersion | 8% by weight based on weight of maskant | Good | None |
| | Rhodamine B Cone 500% | 1% by weight based on weight of maskant | Good | None |
| | Calcofluor RWP | 0.5% and 1% by weight based on weight of maskant | Good | None |
| Immersion of masked part in dye solution | Rhodamine B Cone 500% | 0.1% in methanol | - | None |
| | Pyrafluor White | 0.4% and 0.8% in methanol | - | Strong fluor-escence through pinholes |

SECTION III

METHODIZING OPTIMIZATION TASK

1. APPROACH

Elevated temperature operations in metal working are becoming more prevalent with the increased need for higher strength alloys. Hot forming and heat treating of titanium alloys are necessary to produce quality parts with fully developed physical properties. Less sophisticated cold working procedures are also used to improve the economic attractiveness of titanium alloys.

The sequence by which these parts fit into the chem-mill process can have a great influence on final part quality. This study established the influence of both hot and cold working operations on the performance of existing chem-milling etchants. It also established the best time to chem-mill, thus minimizing distortion and warpage problems. The effect of the optimized method for each operation was checked by determining tensile properties.

Conclusions reached during this study are as follows:

- The particular order in which titanium sheet metal parts are simultaneously hot formed and solution heat treated, quenched, aged, and chem-milled does not affect the degree of distortion, tensile properties, or hydrogen content of Ti-6Al-4V titanium alloy parts. The processing order does, however, affect tensile properties and hydrogen content of Ti-6Al-6V-2Sn titanium alloy parts. Chemical milling prior to aging excessively increases the hydrogen content of these parts.
- Chemical milling either before or after simultaneous forming and aging does not significantly change the amount of distortion incurred in processing or the tensile properties of Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy sheet metal parts. Chemical milling before simultaneous forming and aging, however, considerably increases the hydrogen content of both titanium alloys over that for as-received stock.

- Since chemical milling of Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V titanium alloy sheet metal parts before one-step hot forming does not cause excessive distortion, degrade tensile properties, or increase hydrogen content, it would be less costly to process titanium parts in this manner because maskant scribing (before chem-milling) and net trimming (after chem-milling) could be done on flat parts.
- Dimensional stability and tensile properties of Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V titanium alloy sheet metal parts are not significantly affected by the particular chem-milling/heat treating sequence used. Tensile ultimate and yield strengths of Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy parts are reduced in proportion to the degree to which the parts are chem-milled.
- The change in contour of Ti-8Al-1Mo-1V titanium alloy sheet metal parts caused by chem-milling after room-temperature roll forming or incremental brake forming can be compensated for by overforming the parts a predetermined amount.

2. STUDY AREAS

Chemical milling was evaluated through five different forming/heat treat procedures, each with its own methodizing sequence. The test plan followed is shown in Table XXII.

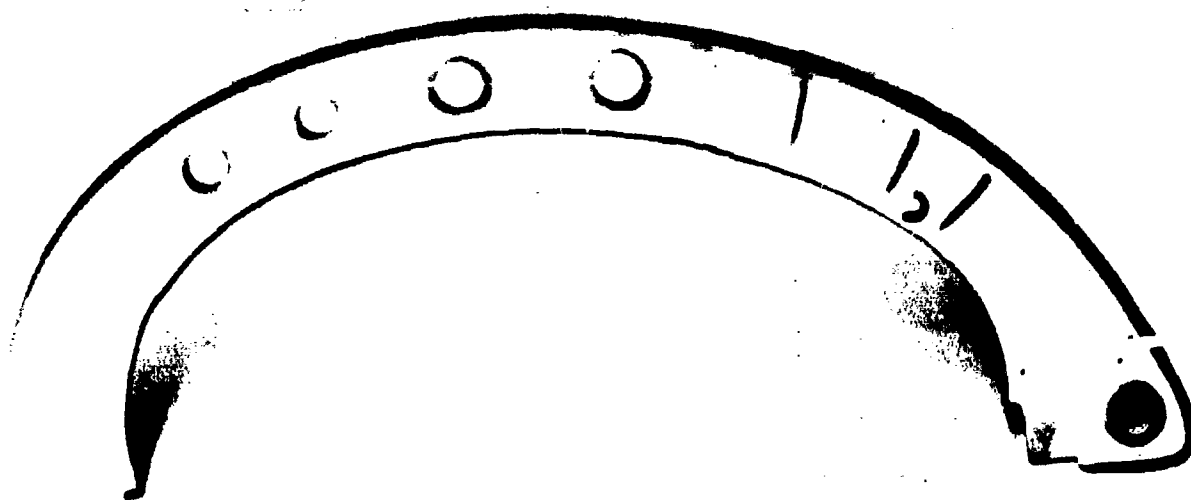
Forming operations studied were:

- Hot forming in 75-ton and 150-ton USI presses
- Cold stretching in a 59-ton Model A-12 Hufford stretch press
- Cold rolling in Farnham rolls and incremental brake forming in a Verson brake.

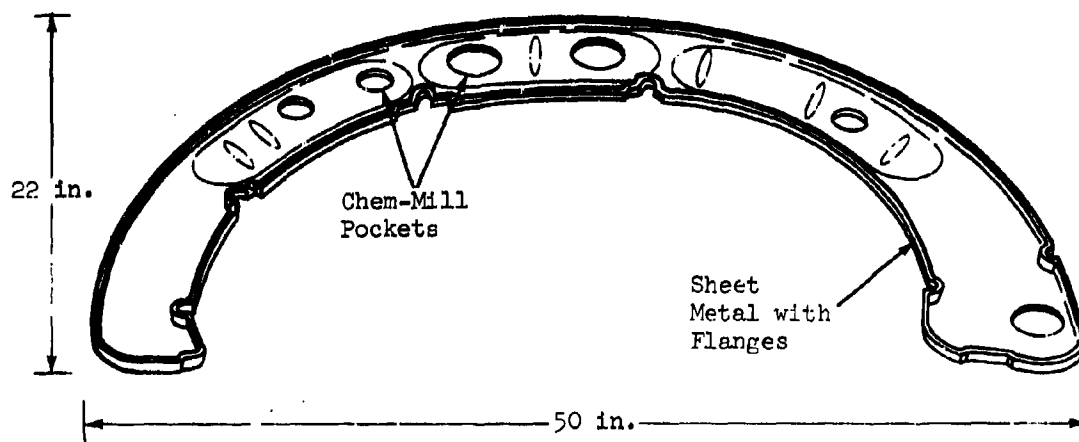
Heat treating was done in existing production heat treat ovens. A 6000-gallon production titanium chem-mill facility and an in-house production flowcoat facility were used for this program. The part selected for study is the typical aircraft structural engine access door frame shown in Figure 58.

The following conditions were checked on completed parts produced by each methodizing sequence:

- Distortion



a. Interior Surface



b. Schematic layout

Figure 58 Hot-Formed Titanium Engine Access Door Frame with Chem-Milled Pockets

TABLE XXII TEST PROCEDURES - TITANIUM FORMING STUDY

| Procedure | Test No. | Alloys | Samples | Operations |
|---------------------------|----------|-----------------------------|---|--|
| Solution Treat Forming | 1 | Ti6-4 Ti6-6-2 | 4/Operation 4/Operation | Chem-mill; form; solution treat; LN ₂ quench; age |
| | 2 | Ti6-4 Ti6-6-2 | 4/Operation 4/Operation | Form; solution treat; LN ₂ quench; chem-mill; age |
| | 3 | Ti6-4 Ti6-6-2 | 4/Operation 4/Operation | Form; solution treat; LN ₂ quench; age; chem-mill |
| Simultaneous Form and Age | 4 | Ti6-4 Ti6-6-2 | 4/Operation 4/Operation | Chem-mill; simultaneous form and age |
| | 5 | Ti6-4 Ti6-6-2 | 4/Operation 4/Operation | Simultaneous form and age; chem-mill |
| Sheet Forming Titanium | 6 | Ti6-4 Ti6-6-2 Ti8-1-1 | 4/Operation 4/Operation 4/Operation | Chem-mill; trim; hot form |
| Furnace Heat Treatment | 7 | Ti6-4 | 8 | Chem-mill before and after age |
| | 8 | Ti6-4 | 8 | Chem-mill before and after stress relieve |
| | 9 | Ti6-4 | 4 | Stress relieve; chem-mill and age |
| | 10 | Ti6-4 | 4 | Stress relieve; age and chem-mill |
| | 11 | Ti6-6-2 | 8 | Chem-mill before and after age |
| | 12 | Ti8-1-1 | 8 | Chem-mill before and after duplex anneal |
| | 13 | Ti6-4 Ti6-6-2 Ti8-1-1 | 4 4 4 | Chem-mill after stretching |
| | 14 | Ti8-1-1 | 4 | Chem-mill after rolling |
| Cold Working | 15 | Ti8-1-1 | 4 | Chem-mill after incremental brake forming |

- Surface finish/line definition in chem-milled areas
- Hydrogen absorption (spot checks)
- Tensile and metallurgical properties

3. CHEMICAL MILLING/SOLUTION HEAT TREATING-FORMING EVALUATION

a. Procedure

In this operation (see Test Numbers 1, 2, and 3 of Table XXII), the Ti-6Al-6V-2Sn and Ti-6Al-4V titanium alloy sheet specimens were processed in accordance with the detailed methodizing procedures listed in Table XXIII in order to establish the optimum procedure that would produce formed, chem-milled, and fully heat-treated parts. All Test No. 1 panels were chem-milled to a depth of 0.030 inch in three pockets using 10 percent hydrofluoric acid etchant at a temperature of 105°F. Four parts were cut from a 36 x 108-inch titanium alloy panel that had been previously chem-milled. All of the 0.070-inch-thick Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy parts for Test Numbers 1, 2, and 3 were coated with Turco and Formkote T-50 lubricants prior to forming. These parts were then hot formed on the 150-ton U.S.I.-Clearing press (Figure 59) using the times, temperatures, and procedures listed in Table XXIV. A ram pressure of 65 tons and bed cushion and slide cushion pressures of 800 psi were used. The complete forming sequence used is shown in Figures 60 through 63. The Incoloy 802 forming die used is shown in Figure 64. Solution heat treating of the Ti-6Al-6V-2Sn titanium alloy parts was performed simultaneously with hot forming at 1400°F-1450°F using a soak time of seven minutes. All of the Ti-6Al-4V titanium alloy parts were formed at 1340°F using a soak time of seven minutes. Since the Ti-6Al-4V titanium alloy solution heat treating temperature is 1675°F, the test parts could not be solution heat treated during forming. Instead these parts were solution heat treated in an air furnace in a holding fixture. Before the Ti-6Al-4V titanium alloy panels were solution heat treated, the following preliminary test was conducted to establish an adequate fixturing technique:

Six engine access door frames were formed from 0.070-inch-thick Ti-6Al-4V titanium alloy sheet, coated with lubricant, wired to a hanger-shaped stainless steel fixture, and hung in an air furnace at 1675°F for ten minutes. Insufficient support during the long heat treat cycle caused the frames to droop and/or creep and become distorted.

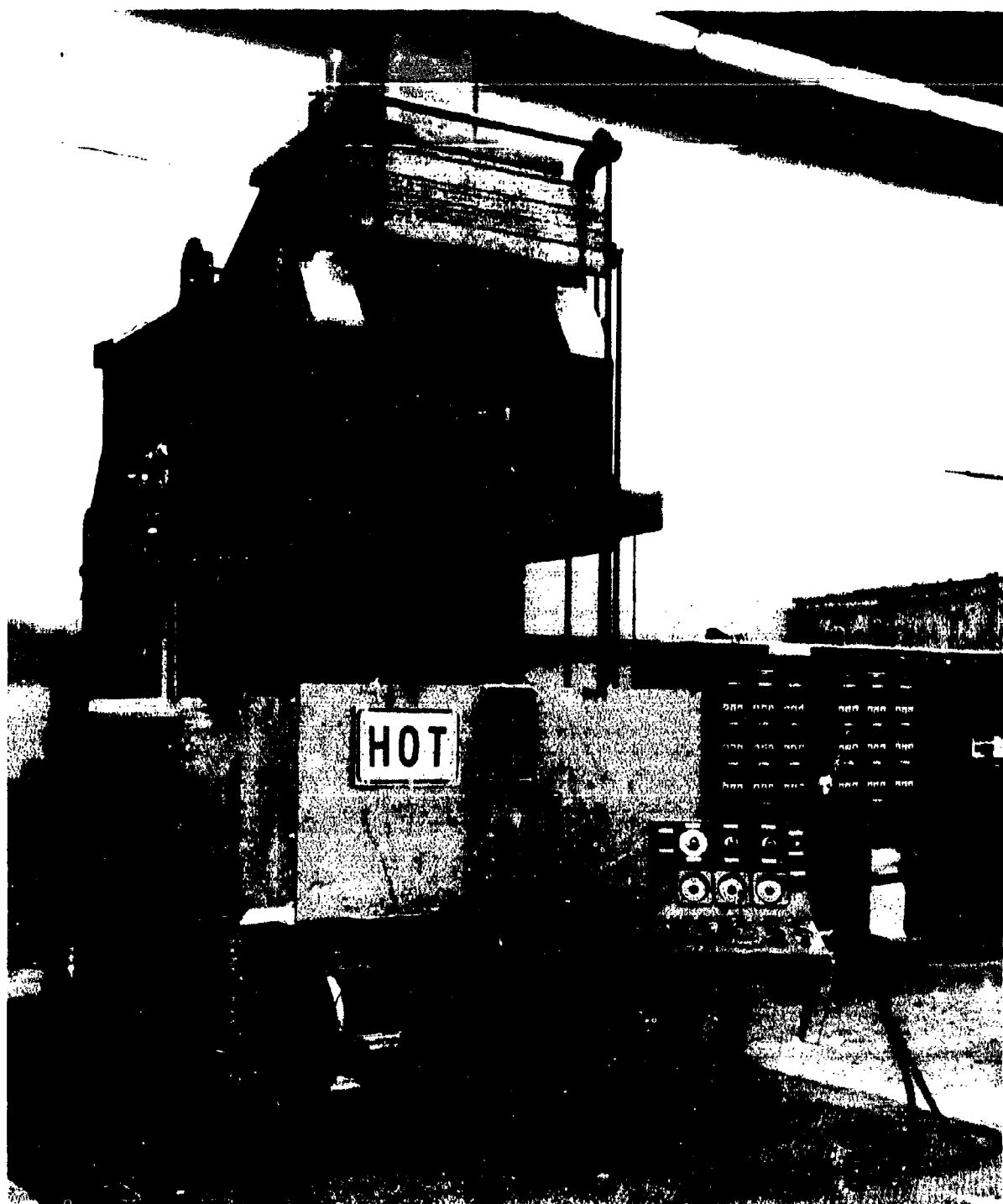


Figure 59 New 150-Ton U.S.I.-Clearing Hot Forming Press

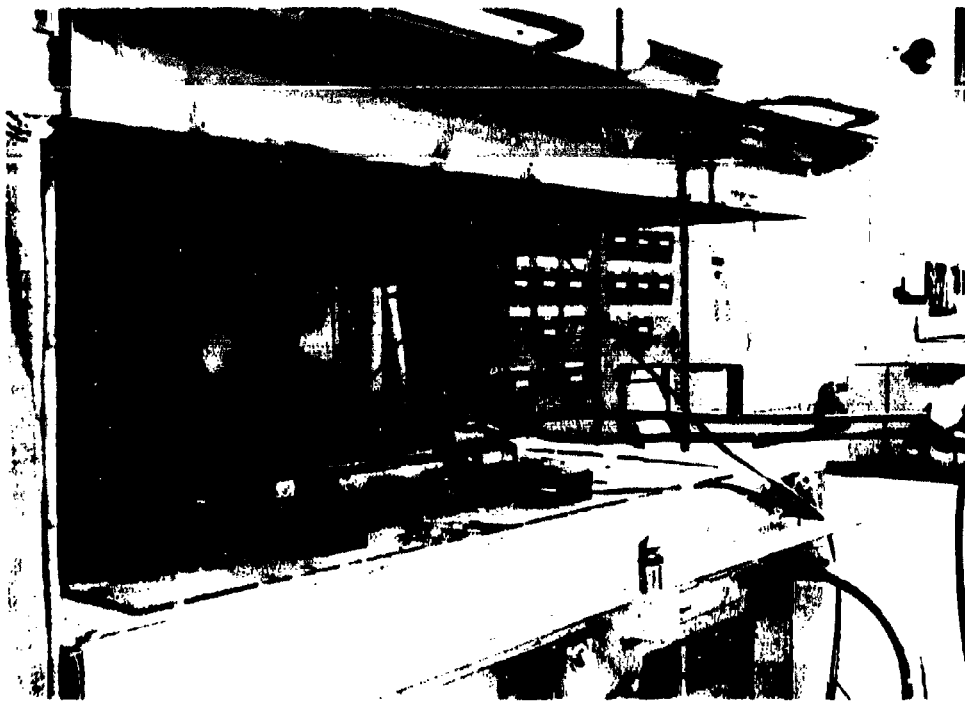


Figure 60 Part Blank Being Positioned On Center Pin

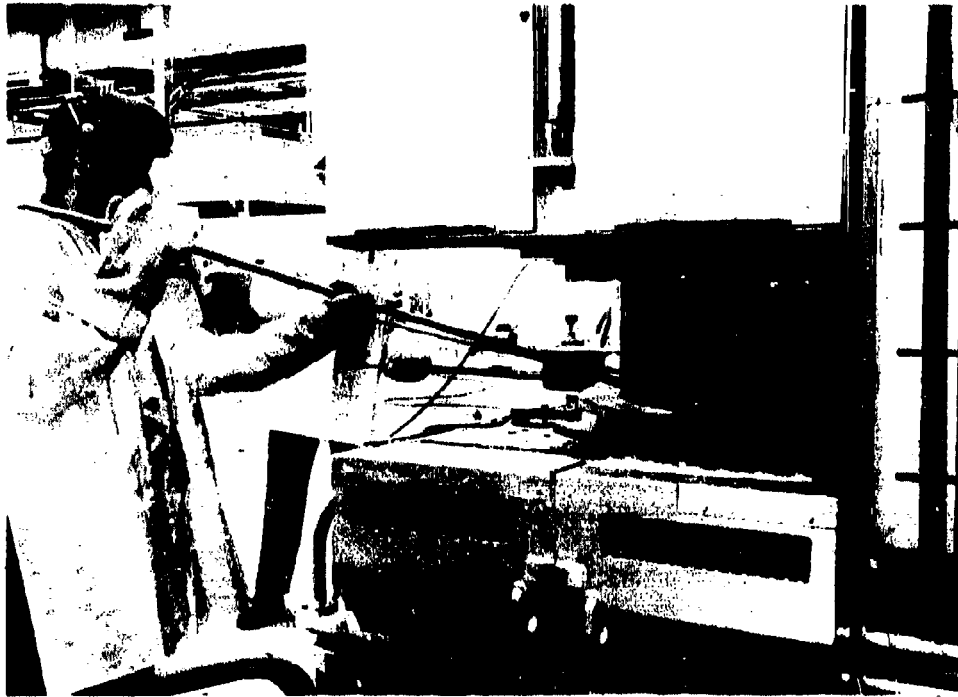


Figure 61 Part Blank Being Positioned On End Pins



Figure 62 Formed Part Being Removed From Male Die

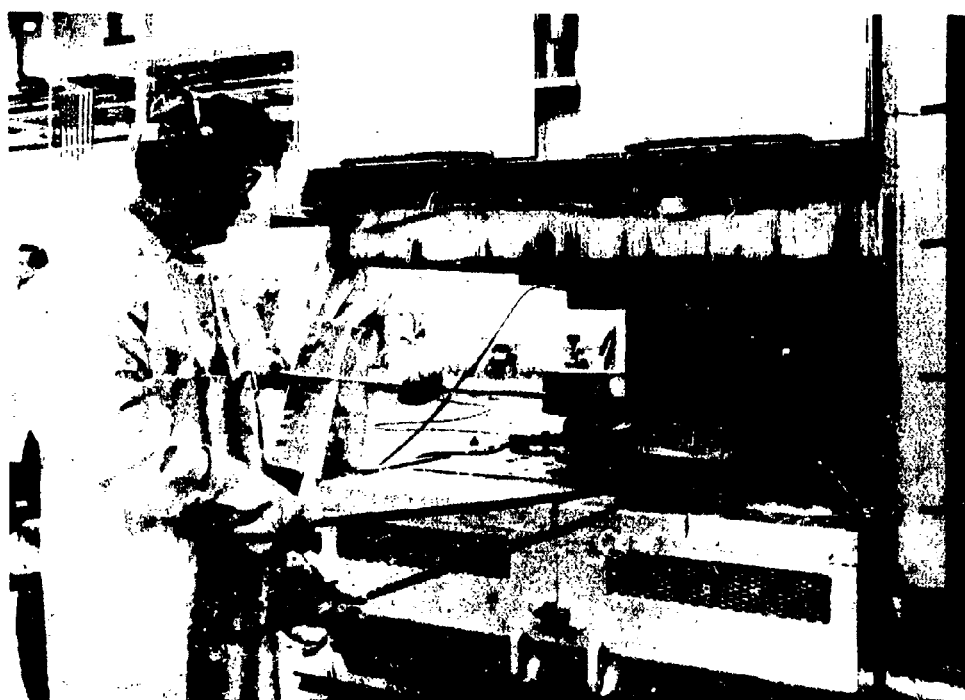


Figure 63 Formed Part Being Removed From the U.S.L.-Clearing Press



(Male)



(Female)

Figure 64 Forming Die

A light stainless steel heat treating fixture (Figure 65) was designed to eliminate such distortion. Since the fixture straddled the frame and was loosely attached to it by means of tapered plugs, it provided multipoint support during transfer of the part to the liquid nitrogen quenching tank (Figure 66). In an attempt to eliminate creep, the fixtured frames were placed on a flat, 1.5-inch-thick steel hearth that provided uniform support and easy handling. All of the Ti-6Al-4V titanium alloy parts for Test Numbers 1, 2, and 3 were solution heat treated for ten minutes at 1675°F and then quenched in liquid nitrogen. The Ti-6Al-6V-2Sn and Ti-6Al-4V titanium alloy parts for Test Numbers 1, 2 and 3 were aged for four hours at 1050°F and 900°F, respectively, at the point in the test cycle shown in Table XXIII.

b. Results

Distortion measurements for the Ti-6Al-6V-2Sn and Ti-6Al-4V titanium alloy frames processed per Test Numbers 1, 2 and 3 are presented in Tables XXV and XXVI, respectively. The degree of distortion of the Ti-6Al-6V-2Sn titanium alloy frames was about the same for all three methodizing procedures (Test Numbers 1, 2 and 3) with the single exception of Part No. RDM-14981-4B which was severely distorted. Solution heat treatment of this part at 1450°F on the forming die caused the part to warp under its own weight. This could have been prevented if the die had been designed so that the parts could have been formed with the flanges up. The parts could then have been easily removed from the die by simply sliding them off onto a flat surface. Examination of the parts for chem-milling characteristics showed a surface finish of 30 to 40 rms and good line definition. The degree of distortion of the Ti-6Al-4V titanium alloy frames was also about equivalent for the three methodizing procedures studied. Although the overall amount of distortion was greater than that for the Ti-6Al-6V-2Sn titanium alloy frames, it was not excessive considering the high solution heat treating temperature (1675°F) and the heat treating holding fixture used.

Tensile specimens were cut from the chem-milled areas of the frames, machined to the configuration shown in Figure 67 and tested. Hydrogen content of the frames before and after processing was also determined. Data obtained are presented in Table XXVII. The Ti-6Al-6V-2Sn titanium alloy frames subjected to the methodizing procedures of Test Numbers 1 and 3 (Part Numbers RDM 14981-1B and -4B and RDM 14983-1A and -4A) had the highest level of tensile properties.

TABLE XXIII

**SOLUTION HEAT TREATING/FORMING-METHODIZING OPERATIONS
FOR Ti-6Al-4V AND Ti-6Al-6V-2 Sn TITANIUM ALLOY TEST PIECES**

| Test No. 1 | Test No. 2 | | | | | | | | | | | | | | | | | | |
|--|------------|----------------|----------------|--|--|--------|---|------|-------------|--|-----|-----|----------------|--|--|--------|---|------|-------------|
| <p>Cut to 36 x 108 = 4 pc. Drill tooling and hang holes Metal stamp P/N in windows per attached route cards Deburr Prepare for chem-mill/solvent clean Solvent clean Mask-organocerams # 1-1010 Bake curing 250°F ± 50°F 30-45 min.</p> <p>Scribe mask for chem-mill area Check and repair voids in mask</p> <p>Chem-mill Ti-6Al-6V-2 Sn Mat'l. Ti-6-4 Cond. anneal. Etching sequence</p> <table><tr><th>No.</th><th>Cut</th><th>Remain. Thick.</th></tr><tr><td></td><td></td><td>+ .000</td></tr><tr><td>1</td><td>.028</td><td>.046 - .005</td></tr></table> <p>Remove remaining mask by hand</p> <p>Inspect Scribe and trim</p> <p>Deburr</p> <p>Solvent clean Turco pretreat Lubricant form kote T50</p> <p>Hot form/solution treat Ti-6Al-4V Liquid nitrogen quench Ti-6Al-6V-2 Sn Air quench</p> <p>Drill (6) #30 pilot holes for lightening holes Blank (6) lightening holes Age to (sta) condition Descale and clean Inspect Distortion check - RMS -</p> | No. | Cut | Remain. Thick. | | | + .000 | 1 | .028 | .046 - .005 | <p>Cut to 36 x 108 = 4 pc. Drill tooling holes only.</p> <p>Metal stamp P/N in windows per attached route cards Deburr Scribe and trim/omit all lightening holes Deburr</p> <p>Solvent clean Turco pretreat Lubricant form kote T50</p> <p>Hot form/solution treat Ti-6Al-4V Liquid nitrogen quench (LN₂) Ti-6Al-6V-2 Sn Air quench</p> <p>Inspect/distortion check Descale and clean</p> <p>Inspect</p> <p>Prepare for chem-mill Solvent clean</p> <p>Mask-organocerams # 1-1010 Bake curing - 250°F ± 50° 30 - 45 min.</p> <p>Scribe mask for chem-mill area Check and repair voids in mask Chem-mill Ti-6Al-6V-2 Sn Mat'l. Ti-6Al-4V cond. (st) Ti-6Al-4V Etching sequence</p> <table><tr><th>No.</th><th>Cut</th><th>Remain. Thick.</th></tr><tr><td></td><td></td><td>+ .000</td></tr><tr><td>1</td><td>.028</td><td>.046 - .005</td></tr></table> <p>Remove remaining mask by hand Inspect Drill (6) pilot holes for lightening holes Blank out (6) lightening holes Deburr Inspect Lubricant form kote T50 Age to (sta) condition Descale and clean Inspect Distortion check - RMS -</p> | No. | Cut | Remain. Thick. | | | + .000 | 1 | .028 | .046 - .005 |
| No. | Cut | Remain. Thick. | | | | | | | | | | | | | | | | | |
| | | + .000 | | | | | | | | | | | | | | | | | |
| 1 | .028 | .046 - .005 | | | | | | | | | | | | | | | | | |
| No. | Cut | Remain. Thick. | | | | | | | | | | | | | | | | | |
| | | + .000 | | | | | | | | | | | | | | | | | |
| 1 | .028 | .046 - .005 | | | | | | | | | | | | | | | | | |

TABLE XXIII

HEAT TREATING/FORMING-METHODIZING OPERATIONS

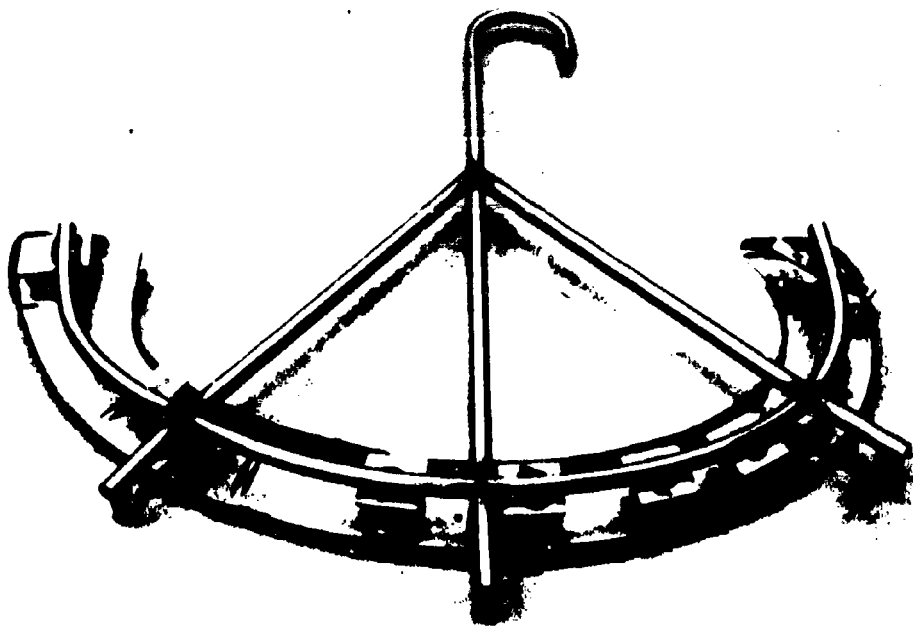
4V AND Ti-6Al-6V-2 Sn TITANIUM ALLOY TEST PIECES

| Test No. 2 | Test No. 3 |
|---|---|
| Cut to 36 x 108 = 4 pc. Drill tooling holes only. | Cut to 36 x 108 = 4 pc. Drill tooling holes only. |
| Metal stamp P/N in windows per attached route cards Deburr Scribe and trim/omit all lightening holes Deburr | Metal stamp P/N in windows per attached route cards Deburr Scribe and trim/OMIT all lightening holes Deburr |
| Solvent clean Turco pretreat Lubricant form kote T50 | Solvent clean Turco pretreat Lubricant form kote T50 |
| Hot form/solution treat Ti-6Al-4V Liquid nitrogen quench (LN ₂) Ti-6Al-6V-2 Sn Air quench | Hot form/solution treat Ti-6Al-4V Liquid nitrogen quench Ti-6Al-6V-2 Sn Air quench |
| Inspect/distortion check Descale and clean | Age to (sta) condition Inspect/distortion check Descale and clean |
| Inspect | Inspect |
| Prepare for chem-mill Solvent clean | Prepare for chem-mill Solvent clean |
| Mask-organocerams # 1-1010 Bake curing - 250°F ± 5° 30 - 45 min. | Mask-organoceram # 1-1010 Bake curing - 250°F ± 5° 30-45 min. |
| Scribe mask for chem-mill area Check and repair voids in mask Chem-mill Ti-6Al-6V-2 Sn Mat'l. Ti-6Al-4V cond. (st) Ti-6Al-4V | Scribe mask for chem mill area Check and repair voids in mask Chem-mill Ti-6Al-4V Mat'l. Ti-6Al-6V-2 Sn cond. anneal |
| Etching sequence No. Cut Remain. Thick. + .000 1 .028 .046 - .005 | Etching sequence No. Cut Remain. Thick. + .000 1 .028 .046 - .005 |
| Remove remaining mask by hand Inspect Drill (6) pilot holes for lightening holes Blank out (6) lightening holes Deburr Inspect Lubricant form kote T50 Age to (sta) condition Descale and clean Inspect Distortion check - RMS - | Remove remaining mask by hand Drill (6) pilot holes for lightening holes Blank out (6) lightening holes Deburr Inspect/distortion check |

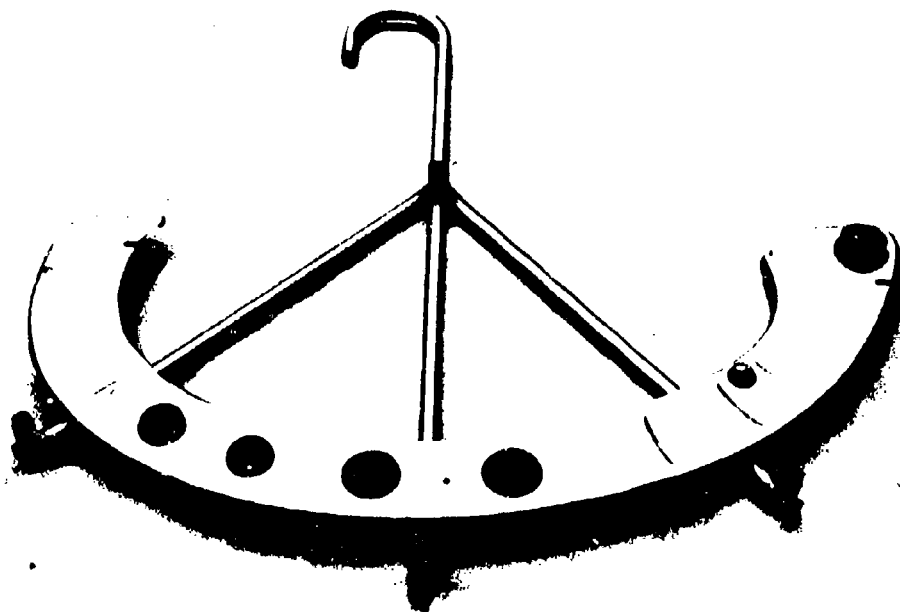
B

TABLE XXIV
SOLUTION HEAT TREAT FORMING TEST SUMMARY

| Test No. | Part No. | Alloy | Temp, °F | Soak Time | Operations |
|----------|----------|--------------------|----------|-----------|---|
| 1 | 1B | Ti-6Al-6V-2Sn ↓ | 1400 | 7 min. | Chem mill; Form; Solution Treat; Air Quench; Age |
| | 2B | | 1400 | | |
| | 3B | | 1400 | | |
| | 4B | | 1450 | | |
| 1 | 1A | Ti-6Al-4V ↓ | 1340 | | Chem mill; Form; Solution Treat; LN ₂ Quench; Age |
| | 2A | | ↓ | | |
| | 3A | | ↓ | | |
| | 4A | | ↓ | | |
| 2 | 1B | Ti-6Al-6V-2Sn ↓ | 1425 | | Form; Solution Treat Air Quench; Chem-Mill; Age |
| | 2B | | 1400 | | |
| | 3B | | 1400 | | |
| | 4B | | 1425 | | |
| 2 | 1A | Ti-6Al-4V ↓ | 1340 | | Form; Solution Treat; LN ₂ Quench; Chem-Mill; Age |
| | 2A | | ↓ | | |
| | 3A | | ↓ | | |
| | 4A | | ↓ | | |
| 3 | 1A | Ti-6Al-6V-2Sn ↓ | 1400 | | Form; Solution Treat; Air Quench; Age; Chem- Mill |
| | 2A | | 1450 | | |
| | 3A | | 1400 | | |
| | 4A | | 1400 | | |
| 3 | 1B | Ti-6Al-4V ↓ | 1340 | | Form; Solution Treat; LN ₂ Quench; Age; Chem- Mill |
| | 2B | | ↓ | | |
| | 3B | | ↓ | | |
| | 4B | | ↓ | | |



(Normal Position)



(View Showing Tapered Plugs in Place)

Figure 65 Solution Heat Treating Quenching Fixture



Figure 66 Cryogenic Quenching of Hot Formed Engine Access Door Frame in Liquid Nitrogen

TABLE XXX

HEIGHT MEASUREMENTS OF CHEM-MILLED/SOLUTION HEAT TREAT FORMED Ti-CAL-V-2Sr FRAMES

| TITANIUM ALLOY | OPERATION SEQUENCE* | TIME OF MEASUREMENT | PANEL NUMBER | RELATIVE HEIGHT AT INSPECTION POINTS, MILS | | | | | | | | Max Change at Eight Points, mils |
|----------------|---------------------|---------------------|--------------|--|------|------|-------|------|------|-------|------|----------------------------------|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Ti-CAL-V-2Sr | I | After Aging | RDM-14981-1B | 0 | -19 | -2 | -41 | -101 | -13 | -18 | -2 | 107 |
| | | | RDM-14981-2B | 0 | -30 | -2 | -78 | -93 | - | -2 | -64 | 85 |
| | | | RDM-14981-3B | 0 | +10 | +7 | -5 | -11 | +5 | - | +14 | 25 |
| | | | RDM-14981-4B | 0 | -400 | -960 | -1163 | -661 | -735 | -1093 | -910 | 1163 |
| Ti-CAL-V-2Sr | II | After Aging | RDM-14982-1B | 0 | -23 | -90 | -106 | -20 | +20 | -40 | +93 | 196 |
| | | | RDM-14982-2B | 0 | -6 | -20 | -7 | -22 | +38 | -19 | -20 | 60 |
| | | | RDM-14982-3B | 0 | +88 | +78 | +103 | -54 | -76 | +65 | +41 | 179 |
| | | | RDM-14982-4B | 0 | -39 | -80 | -92 | -59 | -29 | -66 | +31 | 123 |
| Ti-CAL-V-2Sr | III | After Chem-Milling | RDM-14983-1A | 0 | +12 | -56 | -9 | -93 | -27 | -101 | -76 | 113 |
| | | | RDM-14983-2A | 0 | +46 | 26 | -27 | +54 | +49 | +108 | -2 | 110 |
| | | | RDM-14983-3A | 0 | +25 | -21 | -16 | -1 | +36 | +12 | +64 | 85 |
| | | | RDM-14983-4A | 0 | -38 | -31 | +3 | -99 | -85 | -91 | -24 | 102 |

* I Chem-Mill/Form/Solution Treat-Air Quench/Age
 II Form/Solution Treat-Air Quench/Chem-Mill/Age
 III Form/Solution Treat-Air Quench/Age/Chem-Mill

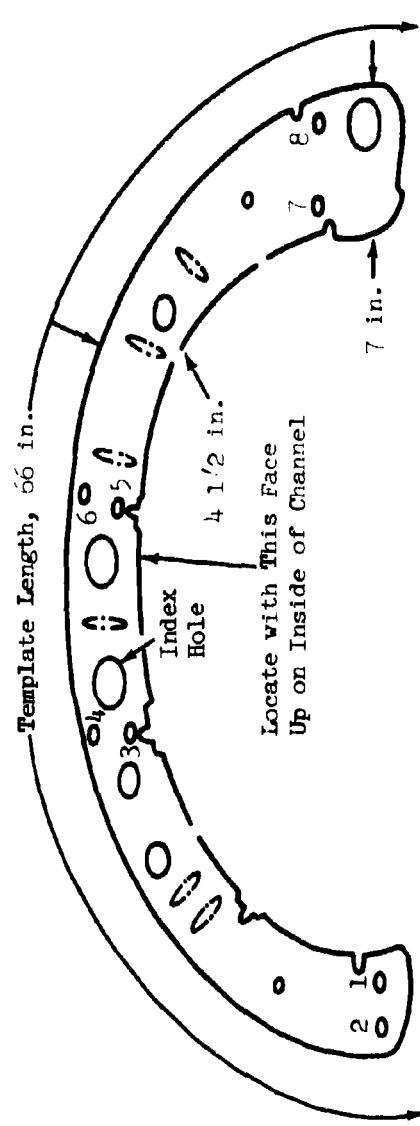
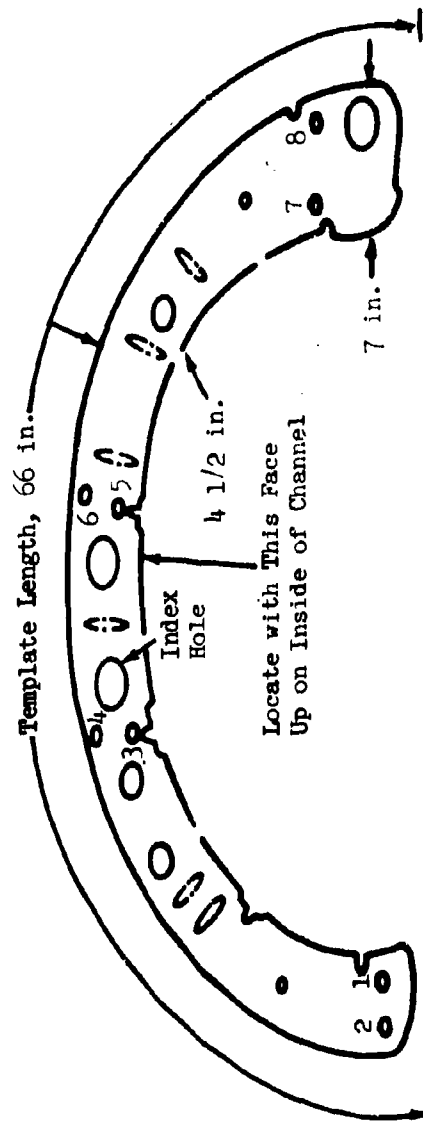


TABLE XXVI HEIGHT MEASUREMENTS OF CHEM-MILLED/SOLUTION HEAT TREAT FORMED TI-6AL-4V FRAMES

| Titanium Alloy | Oper. Seq. | Time Of Meas. | Panel Number | Relative Height at Inspection Points, Mils. | | | | | | | | Max. Chg @ 8 Pts. |
|----------------|------------|--------------------|--------------|---|------|------|------|------|------|------|------|-------------------|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Ti-6Al-4V | I | After Aging | RDM14981-1A | 0 | +34 | +31 | +18 | +13 | -36 | +91 | +290 | 326 |
| | | | RDM14981-2A | 0 | -8 | +17 | +18 | +21 | -10 | +47 | +222 | 232 |
| | | | RDM14981-3A | 0 | +1 | +77 | +42 | -34 | +21 | +26 | +39 | 121 |
| | | | RDM14981-4A | 0 | +60 | +100 | +49 | +192 | +20 | +158 | +398 | 398 |
| Ti-6Al-4V | II | After Aging | RDM14982-1A | 0 | -77 | -67 | -122 | -216 | -240 | -268 | -146 | 268 |
| | | | RDM14982-2A | 0 | -157 | -251 | -314 | -394 | -454 | -335 | -246 | 454 |
| | | | RDM14982-3A | 0 | +16 | +77 | +74 | +1 | -8 | +39 | +33 | 85 |
| | | | RDM14982-4A | 0 | +7 | -5 | +21 | -9 | -9 | +104 | -9 | 113 |
| Ti-6Al-4V | III | After Chem-Milling | RDM14983-1B | 0 | -35 | +65 | +84 | -54 | -16 | +108 | +96 | 162 |
| | | | RDM14983-2B | 0 | +17 | +202 | +99 | +86 | +38 | +204 | +321 | 321 |
| | | | RDM14983-3B | 0 | +41 | +92 | +50 | +274 | +121 | +794 | +615 | 794 |
| | | | RDM14983-4B | 0 | +17 | +98 | +112 | -6 | +11 | +156 | +212 | 218 |

* I Chem-Mill/Form/Solution Treat- LN_2 Quench/Age
 II Form/Solution Treat- LN_2 Quench/Chem-Mill/Age
 III Form/Solution Treat- LN_2 Quench/Age/Chem-Mill



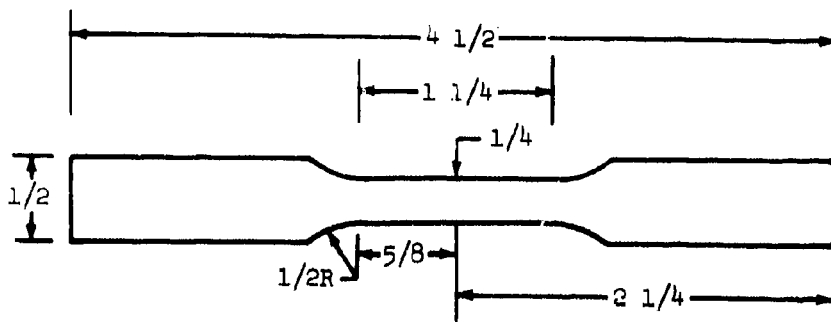


Figure 67 TGS 5350 Tensile Specimen

TABLE XXVII
TENSILE PROPERTIES AND HYDROGEN CONTENT OF TITANIUM ALLOY ENGINE
ACCESS DOOR FRAMES PROCESSED BY VARIOUS METHODIZING PROCEDURES

| Specimen No. | Titanium Alloy | Part Thickness inches | Basic Fab Proc | Processing History* | TENSILE PROPERTIES | | | | | | H ₂ Content, ppm | |
|--------------|----------------|-----------------------|----------------|---------------------|--------------------|------------|---------------|------------|----------------|------------|-----------------------------|------------------|
| | | | | | ULT. STR. ksi | | YIELD STR ksi | | ELONG, percent | | As Rec'd | After Processing |
| | | | | | As Rec'd | After Proc | As Rec'd | After Proc | As Rec'd | After Proc | | |
| 14981-1A | Ti-6-4 | 0.042 | Solution | CM, F, ST, A | 146.0 | 157.1 | 142.0 | 149.7 | 13 | 11 | 102 | 132 |
| 14981-4A | Ti-6-4 | 0.043 | Heat- | CM, F, ST, A | 146.0 | 154.0 | 142.0 | 152.0 | 13 | 11 | 102 | 99 |
| 14981-3B | Ti-6-6-2 | 0.043 | Treat- | CM, F, ST, A | 171.0 | 157.0 | 152.0 | 153.9 | 13 | 12 | 110 | 121 |
| 14981-4B | Ti-6-6-2 | 0.041 | Forming | CM, F, ST, A | 171.0 | 206.8 | 152.0 | 190.2 | 13 | 11 | 110 | 110 |
| 14982-1B | Ti-6-6-2 | 0.046 | | F+ST, CM, A | 171.0 | 157.9 | 152.0 | 152.9 | 13 | 11 | 110 | 375 |
| 14982-4B | Ti-6-6-2 | 0.044 | | F+ST, CM, A | 171.0 | 151.4 | 152.0 | 138.7 | 13 | 15 | 110 | 414 |
| 14983-1A | Ti-6-6-2 | 0.042 | | F+ST, A, CM | 171.0 | 183.3 | 152.0 | 182.9 | 13 | 11 | 110 | - |
| 14983-4A | Ti-6-6-2 | 0.043 | | F+ST, A, CM | 171.0 | 167.0 | 152.0 | 165.4 | 13 | 13 | 110 | 123 |
| 14983-1B | Ti-6-4 | 0.049 | | F, ST, A, CM | 146.0 | 161.2 | 142.0 | 151.2 | 13 | 13 | 102 | 86 |
| 14983-4B | Ti-6-4 | 0.050 | | F, ST, A, CM | 146.0 | 152.4 | 142.0 | 146.4 | 13 | 15 | 102 | - |
| 14984-2A | Ti-6-6-2 | 0.044 | Simul. | CM, F, A | 175.0 | 215.5 | 174.0 | 207.2 | 14 | ** | 118 | >1,310 |
| 14984-4A | " | 0.044 | Forming | CM, F, A | 175.0 | 164.4 | 174.0 | 155.1 | 14 | 11 | 118 | 1,222 |
| 14984-1B | Ti-6-4-ST | 0.050 | And | CM, F, A | 153.0 | 128.2 | 125.0 | 120.5 | 13 | 16 | 79 | 91 |
| 14984-3B | Ti-6-4-ST | 0.052 | Aging | CM, F, A | 153.0 | 161.0 | 125.0 | 149.1 | 13 | 12 | 79 | 112 |
| 14985-1A | Ti-6-6-2 | 0.045 | | F+ST, CM | 175.0 | 183.2 | 174.0 | 179.6 | 14 | 11 | 118 | 200 |
| 14985-2A | Ti-6-6-2 | 0.045 | | F+ST, CM | 175.0 | 178.4 | 174.0 | 174.6 | 14 | 12 | 118 | 206 |
| 14985-3A | Ti-6-6-2 | 0.044 | | F+ST, CM | 175.0 | 163.6 | 174.0 | 161.7 | 14 | 12 | 118 | 178 |
| 14985-4A | Ti-6-6-2 | 0.044 | | F+ST, CM | 175.0 | 177.3 | 174.0 | 171.8 | 14 | ** | 118 | 95 |
| 14986-1A | Ti-6-4 | 0.043 | One-Step Hot | CM, F, F | 146.0 | 133.6 | 142.0 | 133.4 | 13 | 13 | 102 | 78 |
| 14986-3A | Ti-6-4 | 0.044 | Forming | CM, T, F | 146.0 | 139.1 | 142.0 | 137.2 | 13 | 12 | 102 | 86 |
| 14986-1B | Ti-6-6-2 | 0.045 | | CM, T, F, PH | 171.0 | 156.6 | 162.0 | 154.8 | 13 | 11 | 110 | 146 |
| 14986-4B | Ti-6-6-2 | 0.045 | | CM, T, F, PH | 171.0 | 171.4 | 162.0 | 163.4 | 13 | 12 | 110 | 133 |
| 14986-2C | Ti-8-1-1 | 0.046 | | CM, T, F | 143.0 | 139.7 | 129.0 | 131.6 | 14 | 15 | 113 | 136 |
| 14986-4C | " | 0.045 | | CM, T, F | 143.0 | 135.9 | 129.0 | 123.2 | 14 | 12 | 113 | 101 |

* Symbol definitions are as follows: CM-chem-mill; ST-solution heat treat Ti-6Al-4V for 10 minutes at 1675°F and then quench in liquid nitrogen; A-age Ti-6Al-4V for 4 hours at 900°F and age Ti-6Al-6V-2Sn for 4 hours at 1050°F; F-form Ti-6Al-4V for 7 minutes at 1340°F; F+ST-simultaneously form and solution heat treat Ti-6Al-6V-2Sn at 1400°F-1450°F and then quench in air; F+A-simultaneously form and age Ti-6Al-4V for 40 minutes at 1000°F and Ti-6Al-6V-2Sn for 35 minutes at 1125°F; T-trim; PH-postheat for 2 hours at 950°F.

** Specimens broke outside gage length.

The frames subjected to the Test No. 2 procedure in which chem-milling was performed prior to aging at 1050°F had an excessive amount of hydrogen. Tensile properties and hydrogen content of the Ti-6Al-4V titanium alloy frames did not vary significantly with the three methodizing procedures studied.

4. CHEMICAL MILLING/SIMULTANEOUS FORMING AND AGING EVALUATION

a. Procedure

Titanium alloy parts were processed by the two chemical milling/simultaneous forming and aging methodizing cycles shown in Table XXVII (Test Numbers 4 and 5) in order to determine which sequence of operations gives the least distortion and optimum chemical milling results. The simultaneous forming and aging process, which was developed by Grumman, produces formed and fully aged titanium alloy parts. The Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy sheets were received in the solution heat treated condition. The Test No. 4 parts were cut from 36 x 108-inch, chem-milled sheets and then formed, while the Test No. 5 parts were cut from the 36 x 108-inch as-received sheets, formed, and then chem-milled. All of the parts for both operational sequences were coated with Turco Pretreat and Formkote T50 lubricant. All parts were simultaneously formed and aged on the 150-ton U.S.I.-Clearing press using the die shown in Figure 64. Forming cycles for the Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy parts were three-minute soak/40-minute dwell at 1000°F and three-minute soak/30-minute dwell at 1125°F, respectively. After the formed parts were inspected for distortion, tensile and hydrogen content specimens were cut from the chem-milled areas and submitted for testing.

b. Results

Distortion measurements of the formed and chem-milled panels are summarized in Table XXIX. The data indicate that chem-milling either before or after simultaneous forming and aging does not significantly change the amount of distortion incurred in processing. The high degree of distortion of Part No. RDM 14985-3A was caused by shifting of the part on the die during forming. Since this part was cut from as-received sheet, which has a wavy or irregular surface, it was difficult to securely position it on the die locating pins. This condition was alleviated by installing longer locating pins.

TABLE XXVIII

**SIMULTANEOUS FORMING AND AGING/CHEMICAL MILLING METHODIZING
OPERATIONS FOR Ti-6Al-4V AND Ti-6Al-6V-2Sn TITANIUM ALLOY
TEST PIECES**

| Test No. 4 | Test No. 5 | | | | | | | | | | | | |
|--|------------|--------------------------|-------------------|---|-------|--------------------------|--|-----|-----|------------------|---|-------|--------------------------|
| <ol style="list-style-type: none">1. Cut Four 36 x 108-Inch Pieces2. Drill Tooling and Hang Holes3. Metal Stamp Part Numbers4. Deburr5. Prepare for Chem-Mill/Solvent Clean6. Mask (Organoceram No. 1-1010)7. Bake-Cure at 250°F ±5°F for 30-45 Min8. Scribe Mask for Chem-Mill Area9. Check and Repair Voids in Mask10. Chem-Mill Material - $\left\{ \begin{array}{l} \text{Ti-6Al-6V-2Sn} \\ \text{Ti-6Al-4V} \end{array} \right\}$ Solution Heat Treated Condition Etching Sequence <table><tr><td>No.</td><td>Cut</td><td>Remain. Thickness</td></tr><tr><td>1</td><td>0.028</td><td>0.046 + 0.000 - 0.005</td></tr></table>11. Remove Remaining Mask By Hand12. Inspect13. Scribe and Trim (Omit Lightening Holes)14. Deburr15. Solvent Clean16. Turco Pretreat, Lubricant Formkote T5017. Simultaneously Form and Age Ti-6Al-6V-2Sn (35 Min 1125°F) Ti-6Al-6V 40 Min 1000°F)18. Air Cool19. Descale and Clean20. Inspect21. Drill Six No. 30 Pilot Holes for Lightening Holes22. Blank Six Lightening Holes23. Inspect | No. | Cut | Remain. Thickness | 1 | 0.028 | 0.046 + 0.000 - 0.005 | <ol style="list-style-type: none">1. Cut Four 36 x 108-Inch Pieces2. Drill Tooling and Hang Holes3. Metal Stamp Part Numbers4. Deburr5. Scribe and Trim (Omit all Lightening Holes)6. Deburr7. Solvent Clean8. Turco Pretreat, Lubricant Formkote T509. Simultaneously Form and Age Ti-6Al-6V-2Sn (35 Min 1125°F) Ti-6Al-4V (40 Min 1000°F)10. Air Cool11. Descale and Clean12. Inspect13. Prepare for Chem Mill/Solvent Clean14. Mask (Organoceram No. 1-1010)15. Bake - Cure at 250°F ±5°F for 30-45 Min16. Scribe Mask for Chem-Mill Area17. Check and Repair Voids in Mask18. Chem Mill Material- $\left\{ \begin{array}{l} \text{Ti-6Al-6V-2Sn} \\ \text{Ti-6Al-4V} \end{array} \right\}$ Solution Heat Treated and Aged Condition Etching Sequence <table><tr><td>No.</td><td>Cut</td><td>Remain Thickness</td></tr><tr><td>1</td><td>0.028</td><td>0.046 + 0.000 - 0.005</td></tr></table>19. Remove Remaining Mask by Hand20. Inspect21. Drill Six No. 30 Pilot Holes for Lightening Holes22. Blank Six Lightening Holes23. Inspect | No. | Cut | Remain Thickness | 1 | 0.028 | 0.046 + 0.000 - 0.005 |
| No. | Cut | Remain. Thickness | | | | | | | | | | | |
| 1 | 0.028 | 0.046 + 0.000 - 0.005 | | | | | | | | | | | |
| No. | Cut | Remain Thickness | | | | | | | | | | | |
| 1 | 0.028 | 0.046 + 0.000 - 0.005 | | | | | | | | | | | |

TABLE XXIX HEIGHT MEASUREMENTS OF CHEM-MILLED/SIMULTANEOUSLY
FORMED AND AGED TITANIUM ALLOY FRAMES

| Titanium Alloy | Oper. Seq. | Time Of Meas. | Panel Number | Relative Height at Inspection Points, mils | | | | | | | | Max. Chg @ 8 Pts. |
|----------------|------------|--------------------------------------|--------------|--|------|------|------|------|------|------|------|-------------------|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| Ti-6Al-6V-2Sn | IV | After Simultaneously Forming & Aging | RDM14984-1A | 0 | -8 | -43 | -64 | -66 | -33 | -112 | -98 | 112 |
| | | | RDM14984-2A | 0 | -22 | -24 | -56 | +2 | -33 | +28 | +51 | 107 |
| | | | RDM14984-3A | 0 | -66 | -155 | -172 | -128 | +35 | +48 | +100 | 272 |
| | | | RDM14984-4A | 0 | -7 | +115 | +94 | +108 | +27 | +4 | +20 | 122 |
| Ti-6Al-6V-2Sn | V | After Chem-Milling | RDM14985-1A | 0 | +55 | -118 | -107 | -121 | -96 | +53 | -120 | 176 |
| | | | RDM14985-2A | 0 | -3 | -30 | -24 | -55 | -50 | 0 | -29 | 55 |
| | | | RDM14985-3A | 0 | -95 | -766 | -853 | -710 | -673 | -750 | -367 | 853** |
| | | | RDM14985-4A | 0 | -61 | -233 | -259 | -239 | -263 | -134 | -237 | 263 |
| Ti-6Al-4V | IV | After Simultaneously Forming & Aging | RDM14984-1B | 0 | -139 | -233 | -266 | -204 | -262 | -59 | -245 | 268 |
| | | | RDM14984-2B | 0 | -107 | -98 | -106 | -91 | -127 | -56 | -190 | 190 |
| | | | RDM14984-3B | 0 | -106 | -168 | -213 | -127 | -188 | +14 | -163 | 227 |
| | | | RDM14984-4B | 0 | -102 | -169 | -202 | -145 | -199 | -9 | -168 | 202 |
| Ti-6Al-4V | V | After Chem-Milling | RDM14985-1B | 0 | +44 | -127 | -146 | -115 | -149 | +59 | -114 | 193 |
| | | | RDM14985-2B | 0 | -6 | +1 | +7 | -38 | -41 | +15 | -26 | 53 |
| | | | RDM14985-3B | 0 | -175 | -177 | -323 | -109 | -94 | -186 | -72 | 323 |
| | | | RDM14985-4B | 0 | -15 | -160 | -175 | -179 | -214 | -69 | -202 | 202 |

* IV Chem-Mill/Simultaneously Form and Age.

V Simultaneously Form and Age/Chem-Mill.

** Part Shifted on Die

Tensile properties and hydrogen content values for these parts are presented in Table XXVII (Specimen Numbers 14984 and 14985). The data indicate that chemical milling before simultaneous forming and aging considerably increases the hydrogen content of the material over that for the as-received stock. This situation also occurred with the solution heat treated and formed specimens when chemical milling preceded aging.

5. CHEMICAL MILLING/ONE-STEP HOT FORMING EVALUATION

a. Procedure

Tests were conducted to determine the proper operational sequence for processing involving both chemical milling and the Grumman-developed, one-step-hot-forming method which was used in place of the conventional, two-step cold preforming/hot sizing method. The chemical milling pattern for four frame blanks was laid out on 36 x 108-inch Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V titanium alloy sheets which were then chem-milled. The frame blanks were cut out of the chem-milled sheets, given a coating consisting of one part Turco Pretreat and three parts Formkote T-50, and hot formed per the methodizing sequence shown in Table XXX. Forming conditions used for the Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V titanium alloy blanks were 1340°F/3-minute dwell time/7-minute soak time, 1250°F/3-minute dwell time/7-minute soak time, and 1500°F/3-minute dwell time/5-minute soak time, respectively. U.S.I.-Clearing press parameters were a ram pressure of 65 tons, and upper and lower cushion pressures of 800 pounds.

b. Results

Examination of the chem-milled and formed frames showed that the chem-milled pockets were not damaged and had not collapsed. Distortion measurements are summarized in Table XXXI. The Ti-6Al-6V-2Sn titanium alloy frames were less distorted than the Ti-6Al-4V titanium alloy frames. The degree of distortion of the Ti-8Al-1Mo-1V titanium alloy frames was about equivalent to that for the Ti-6Al-6V-2Sn titanium alloy frames except for one frame (No. RDM-14986-2c) which was difficult to remove from the die pins. The lubricant mixture, which had a lubricity equivalent to that for the individual components, adhered to the frames without flaking. It is estimated that a cost savings of 16 cents per square foot could be realized by using the Turco Pretreat/Formkote T-50 lubricant mixture.

Tensile properties and hydrogen content of the processed frames are presented in Table XXVII. All of the Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V titanium alloy specimens met minimum property requirements and did not contain an excessive amount of hydrogen. In summary, it would be less costly to chem-mill titanium parts before they are one-step hot formed because maskant scribing and net trimming (after chemical milling) could be done on flat parts.

TABLE XXV

CHEMICAL MILLING/HOT FORMING METHODIZING OPERATIONS

| Test No. 6 | | | | | | | | | | |
|--|---------------------------------------|---------------------|---------------------|---|------|-------------|--|--|--------|--------|
| Cut | Scribe & Trim | | | | | | | | | |
| Drill Tooling & Hang Holes | Deburr | | | | | | | | | |
| Metal Stamp Part No. in Excess Area | Solvent Clean | | | | | | | | | |
| | Turco Pretreat | | | | | | | | | |
| | Lubricant Form T50 | | | | | | | | | |
| Deburr | Hot Form/ | | | | | | | | | |
| Prepare for Chem-Mill | Inspect | | | | | | | | | |
| Clean/ | | | | | | | | | | |
| Mask-Organoceram #1-1010 | Post Heat at 950°F $\pm 10^\circ$ for | | | | | | | | | |
| Bake Curing 250°F +05°F 30-45 Min | 2 Hrs ± 15 Min. | | | | | | | | | |
| Scribe Mask for C/M Area | Ti-6Al-6V-2Sn only | | | | | | | | | |
| Check and Repair Voids in Mask | Descale & Clean | | | | | | | | | |
| Chem-Mill | Drill (6) Pilot Holes for | | | | | | | | | |
| Material Ti-6Al-6V-2Sn, Ti-6Al-4V, | Lightening Holes | | | | | | | | | |
| Ti-8Al-1Mo-1V Cond. Anneal | Blank Out (6) Lightening Holes | | | | | | | | | |
| Etching Sequence | | | | | | | | | | |
| <table><tr><td><u>No.</u></td><td><u>Cut</u></td><td><u>Remain Thick</u></td></tr><tr><td>1</td><td>.028</td><td>.046 + .000</td></tr><tr><td></td><td></td><td>- .005</td></tr></table> | <u>No.</u> | <u>Cut</u> | <u>Remain Thick</u> | 1 | .028 | .046 + .000 | | | - .005 | Deburr |
| <u>No.</u> | <u>Cut</u> | <u>Remain Thick</u> | | | | | | | | |
| 1 | .028 | .046 + .000 | | | | | | | | |
| | | - .005 | | | | | | | | |
| Remove Remaining Mask by Hand | Inspect | | | | | | | | | |
| Inspect | Distortion Check | | | | | | | | | |
| | RMS | | | | | | | | | |
| (Contd) | | | | | | | | | | |

TABLE XXXI HEIGHT MEASUREMENTS OF
CHEM-MILLED/ONE-STEP HOT FORMED TITANIUM ALLOY FRAMES

| Titanium Alloy | Operation Sequence* | Time of Measurement | Panel Number | Relative Height At Inspection Points, Mils | | | | | | | |
|----------------|---------------------|---------------------|--------------|--|------|------|------|------|------|------|------------|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 Max Ch |
| Ti-6Al-6V-2Sn | I | After Hot Forming | RDM-14986-1B | 0 | -2 | +81 | +70 | +51 | +33 | +55 | +52 83 |
| | | | RDM-14986-2B | 0 | -6 | -3 | -28 | -19 | -64 | -35 | -32 64 |
| | | | RDM-14986-3B | 0 | -5 | -12 | -36 | -12 | -55 | -20 | -28 56 |
| | | | RDM-14986-4B | 0 | -19 | -102 | -99 | -113 | -115 | -57 | -65 115 |
| Ti-6Al-4V | I | After Hot Forming | RDM-14986-1A | 0 | +69 | +193 | +162 | +180 | +151 | +210 | +234 234 |
| | | | RDM-14986-2A | 0 | -14 | -27 | -25 | -40 | -62 | +57 | -10 119 |
| | | | RDM-14986-3A | 0 | -59 | -180 | -209 | -133 | -144 | -168 | -206 209 |
| | | | RDM-14986-4A | 0 | -80 | -63 | -113 | -80 | -97 | -149 | -153 149 |
| Ti-8Al-1Mo-1V | I | After Hot Forming | RDM-14986-1C | 0 | -29 | -32 | -33 | -24 | -34 | +34 | -42 76 |
| | | | RDM-14986-2C | 0 | -274 | +261 | +167 | -82 | -141 | +207 | +525 838** |
| | | | RDM-14986-3C | 0 | +3 | +20 | -31 | +30 | +11 | +144 | +68 154 |
| | | | RDM-14986-4C | 0 | -15 | +54 | +50 | +24 | +9 | +38 | -13 73 |

* Chem-Mill/Trim/Hot Form

** Difficulty in Removing Part From Die

6. CHEMICAL MILLING/HEAT TREATING EVALUATION

a. Procedure

Manufacturing operations involving both chemical milling and heat treating must be properly methodized to minimize part distortion and to prevent degradation of physical properties. Airframe fabricators use heat treatment to recover physical properties degraded by previous shop operations and to upgrade properties of materials. This evaluation was conducted to determine if the sequence of chem-milling/heat treating operations affects the tensile properties and dimensional stability of titanium alloy panels. Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V titanium alloy, 8 x 12-inch panels were chem-milled in two steps before and after heat treating to produce two 3 x 9-inch pockets in each panel having depths of 0.030 and 0.050 inch (see Table XXXII). Tensile specimens having the configuration shown in Figure 67 were machined from both chem-milled pockets in one panel of each four-panel set. Panel distortion was determined by measuring the height at certain points as indicated by an inspection checking fixture (Table XXXIII). All panels were cleaned in an alkaline bath and coated with Turco Pretreat and Formkote T-50 lubricants prior to heat treatment.

Before the chem-milling/heat treating tests were begun, preliminary tests were conducted to optimize the procedure to be used in solution heat treating of Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy panels. During the course of these tests, it was found that the holding fixture did not provide adequate support to the panels in the 1600°F - 1700°F temperature range. These panels exhibited considerable warpage after the solution heat treatment and subsequent water quenching. The holding fixture (Fig. 68) was modified. The height of the fixture was decreased from 29 to 17 inches and screens were replaced by bars to which panels were wired in subsequent heat treatment operations. The grip of the fixture was also modified to provide for easier handling. These modifications resulted in an appreciable decrease in the extent of warpage sustained by panels in the course of solution heat treatment and water quenching operations.

Another series of preliminary tests was conducted to determine thickness of the α -layer in various stages of solution heat treating and aging operations. Hard and brittle-case is caused by diffusion of oxygen into the metal on exposures to temperatures above 1200°F in air furnaces, and can have detrimental effects on material properties. A metallographic specimen was removed from a Ti-6Al-4V titanium alloy test panel

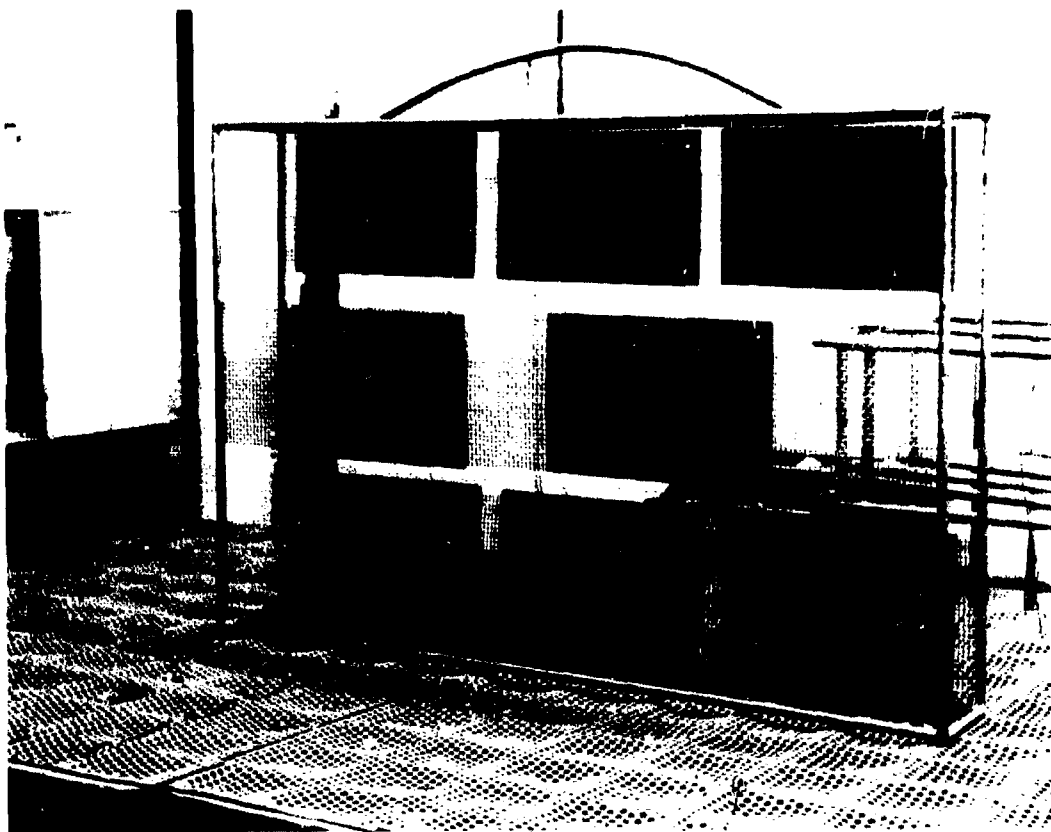


Figure 68 Panels on Heat Treat Fixture Ready for Furnace Aging

TABLE XXXII
CHEMICAL MILLING/HEAT TREATING SUMMARY

| Titanium Alloy (Initial Condition) | Thickness, inches | Operation Sequence | Panels | |
|---------------------------------------|----------------------|---------------------------------------|--------|-----------------|
| | | | Number | Size, inches |
| Ti-6Al-4V Annealed | 0.100 | Chem-Mill*-Solution Heat Treat*-Age* | 4 | 8 x 12 |
| | | *Solution Heat Treat*-Chem Mill -Age* | 4 | 8 x 12 |
| | | *Solution Heat Treat*-Age -Chem Mill* | 4 | 8 x 12 |
| Ti-6Al-4V Solution Heat Treated | 0.070 | Chem Mill*-Age* | 4 | 8 x 12 |
| | | *Age*-Chem Mill* | 4 | 8 x 12 |
| Ti-6Al-6V-2Sn Annealed | 0.065 | Chem Mill*-Solution Heat Treat*-Age* | 4 | 8 x 12 |
| | | *Solution Heat Treat*-Chem Mill -Age* | 4 | 8 x 12 |
| | | *Solution Heat Treat*-Age -Chem Mill* | 4 | 8 x 12 |
| Ti-8Al-1 Mo-1V Duplex Annealed | 0.070 | Chem Mill*-Duplex Anneal* | 4 | 8 x 12 |
| | | *Duplex Anneal*-Chem Mill* | 4 | 8 x 12 |

(* Indicates distortion measurement)

Table XXXIII HEIGHT MEASUREMENTS OF CHEM

| Titanium Alloy | Heat Treat Condition | Thick-ness, in. | Operation Sequence* | Panel No. | Time Of Measurement |
|----------------|-----------------------|-----------------|---------------------|-------------------------------|--------------------------------|
| Ti-6Al-4V | Annealed | 0.100 | I | TCM 69-29-A -B -C -D | After Chem Milling |
| | | | II | -E -F -G -H | Before Sol ution Heat Treating |
| | | | III | -I -J -K -L | Before Sol ution Heat Treating |
| Ti-6Al-4V | Solution Heat Treated | 0.070 | IV | TCM 69-32-A -B -C -D | After Chem Milling |
| | | | V | -E -F -G -H | Before Age |
| Ti-6Al-6V-2Sn | Annealed | 0.065 | I | TCM 69-33-A -B -C -D | After Chem Milling |
| | | | II | -E -F -G -H | Before Sol ution Heat Treating |
| | | | III | -I -J -K -L | Before Sol ution Heat Treating |
| Ti-8Al-1Mo-1V | Annealed | 0.070 | VI | TCM 69-34-A -B -C -D | After Chem Milling |
| | | | VII | -E -F -G -H | Before Duplex Annealing |

| | | |
|--------|--------|--------|
| TCM-69 | | |
| ○ 7 | ○ 8 | ○ 9 |
| ○ 4 | ○ 5 | ○ 6 |
| 0.000 | | |
| ○ 1 | ○ 2 | ○ 3 |

Inspection
Checking
Fixture

* I - Chem-Mill/Solution Heat Treat/Age
II - Solution Heat Treat/Chem-Mill/Age
III - Solution Heat Treat/Age/Chem-Mill
IV - Chem-Mill/Age

V - Age/Chem-Mill
VI - Chem-Mill/Duplex Anneal
VII - Duplex Anneal/Chem-Mill

A

HEIGHT MEASUREMENTS OF CHEM-MILLED/HEAT TREATED TITANIUM PANELS

| Panel No. | Time Of Measurement | Maximum Change At 9 Inspection Points-Mils | Time of Measurement | Maximum Change At 9 Inspection Points-Mils | Time of Measurement | Maximum Change At 9 Inspection Points-Mils |
|-------------|-------------------------------|--|---------------------------|--|---------------------|--|
| TCM 69-29-A | After Chem-Milling | 32 | After Solution Heat Treat | 305 | After Aging | 279 |
| -B | | 33 | | 482 | | 419 |
| -C | | 22 | | 351 | | 289 |
| -D | | 34 | | 364 | | 250 |
| -E | Before Solution Heat Treating | 21 | After Solution Heat Treat | 239 | After Aging | 279 |
| -F | | 15 | | 218 | | 503 |
| -G | | 24 | | 483 | | 255 |
| -H | | 11 | | 329 | | 255 |
| -I | Before Solution Heat Treating | 25 | After Solution Heat Treat | 150 | After Chem-Milling | 126 |
| -J | | 39 | | 354 | | 299 |
| -K | | 47 | | 254 | | 130 |
| -L | | 23 | | 205 | | 225 |
| TCM 69-32-A | After Chem-Milling | 220 | After Aging | 247 | — | — |
| -B | | 375 | | 315 | | |
| -C | | 782 | | 443 | | |
| -D | | 365 | | 362 | | |
| -E | Before Aging | 418 | After Aging | 146 | After Chem-Milling | 132 |
| -F | | 194 | | 127 | | 153 |
| -G | | 246 | | 299 | | 280 |
| -H | | 167 | | 150 | | 175 |
| TCM 69-33-A | After Chem-Milling | 30 | After Solution Heat Treat | 626 | After Aging | 359 |
| -B | | 40 | | 959 | | 294 |
| -C | | 43 | | 525 | | 386 |
| -D | | 30 | | 240 | | 234 |
| -E | Before Solution Heat Treating | 31 | After Solution Heat Treat | 249 | After Aging | 351 |
| -F | | 23 | | 375 | | 503 |
| -G | | 23 | | 689 | | 672 |
| -H | | 82 | | 334 | | 242 |
| -I | Before Solution Heat Treating | 46 | After Solution Heat Treat | 262 | After Chem-Milling | 237 |
| -J | | 59 | | 253 | | 273 |
| -K | | 18 | | 688 | | 458 |
| -L | | 39 | | 281 | | 132 |
| TCM 69-34-A | After Chem-Milling | 65 | After Duplex Anneal | 107 | — | — |
| -B | | 96 | | 140 | | |
| -C | | 52 | | 145 | | |
| -D | | 26 | | 231 | | |
| -E | Before Duplex Annealing | 22 | After Duplex Anneal | 304 | After Chem-Milling | 316 |
| -F | | 34 | | 89 | | 92 |
| -G | | 24 | | 359 | | 353 |
| -H | | 41 | | 127 | | 136 |

V - Age/Chem-Mill
 VI - Chem-Mill/Duplex Anneal
 VII - Duplex Anneal/Chem-Mill

B

which was exposed to 1700°F for 15 minutes and subsequently cleaned in an acid bath. The specimen was mounted in Lucite, polished, etched with 2% HF solution, and examined at 250x magnification. The examination revealed presence of the α -layer (Figure 69). Another metallographic specimen was removed from the same panel after a simulated aging cycle (1000°F for 4 hrs.) and subsequent acid cleaning. Figure 70 shows that the α -layer was removed completely in the course of the second cleaning operation. It should be noted that the cooling rate of this experimental panel was not controlled and that the metallographic specimens were purposely overetched to emphasize the difference of the α -layer from the interior section. Accordingly, the photomicrographs shown in Figures 69 and 70 should not be used to draw conclusions pertaining to the response of the material to heat treatment.

The following heat treating procedures were used:

- Ti-6Al-4V
 - Heat to 1,675°F - 1,725°F and hold for 5-15 minutes
 - Water quench
 - Heat to 1,000°F and hold for 4 hours
 - Air cool
- Ti-6Al-6V-2Sn
 - Heat to 1,550°F - 1,625°F and hold for 5-15 minutes
 - Water quench
 - Heat to 1,100°F for 4 hours
 - Air cool
- Ti-8Al-1Mo-1V
 - Heat to 1,450°F and hold for 8-10 hours
 - Cool at rate of 50°F/hour to 800°F
 - Air cool to room temperature
 - Heat to 1,425°F and hold for 30-60 minutes
 - Air cool

b. Results

Height measurements taken at various steps in the methodizing sequences are summarized in Table XXXIII. Conclusive trends that would indicate the best time for chemical milling could not be drawn from these data. A tendency toward less distortion was indicated in four cases in which chemical milling was performed as a final operation (Panel Numbers TCM 69-29-I and -L, and TCM 69-33-I, and -L).

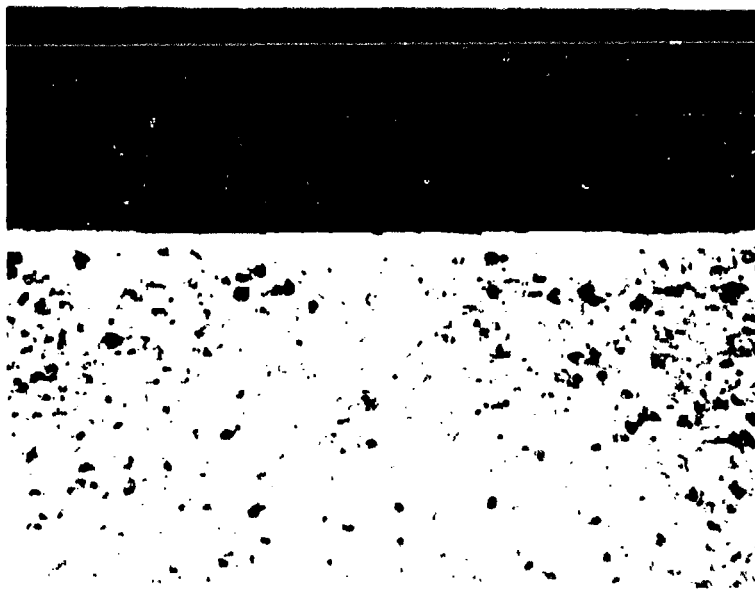


Figure 69 Microsection of Ti-6Al-4V Panel
Showing Alpha Layer (250x Magnification)



Figure 70 Microsection of Ti-6Al-4V Panel
Showing No Alpha Layer (250x Magnification)

The processing history and tensile properties of the titanium alloy specimens are summarized in Table XXXIV. Although the data indicate that variations in the processing sequence have no significant effect on tensile properties of the Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy specimens, the extent to which the specimens were chem-milled proportionately reduced tensile properties. It was also found that ultimate and yield tensile strengths of Ti-8Al-1Mo-1V titanium alloy were slightly reduced by the second reheating operation during duplex annealing (but before chemical milling). Tensile properties of the Ti-8Al-1Mo-1V titanium alloy specimens were not significantly affected by the chemical milling operations.

7. CHEMICAL MILLING/COLD WORKING EVALUATION

a. Procedure

Compared to hot forming, cold or room-temperature working induces a variety of surface stresses in metallic parts depending on the particular technique used (e.g., roll forming, incremental brake forming, or stretching). This study was carried out to determine the amount of overforming needed to compensate for chemical milling effects. The general procedure involved measuring room-temperature-formed parts before and after chemical milling to determine the amount of stress relieving and straightening that had occurred.

- (1) Rolling. Four 18 x 27-inch blanks were cut from a 36 x 108-inch, Ti-8Al-1Mo-1V titanium alloy sheet and rolled on 15-foot-long Farnham rolls to a 70-inch-radius. Two pockets were then chem-milled in the rolled blanks to a depth of 0.035 inch. A typical part is shown in Figure 71. Contour measurements were made after rolling and again after chemical milling. The methodizing sequence followed is shown in Table XXXV.
- (2) Incremental Brake Forming. The material, blank size, and methodizing procedure used were the same as those specified for rolling in Table XXXV. Four blanks were incrementally brake formed to a 70-inch-radius on an 18-foot-long Chicago press brake using a one-inch-radius braking bar.
- (3) Stretch Forming. The RDM-2239, experimental stretch die (Figure 72) was set up on the 59-ton, A-12 Hufford stretch press. A 13 9/16 x 48 x 0.070-inch, Ti-6Al-4V titanium alloy sheet was clamped in the jaws of the press and subjected to an initial load of 35 tons at room temperature. The die failed as the sheet was wrapped around the die. The die failed a second time after being reinforced with two-inch-thick aluminum plate. A production

TABLE XXIV
PROCESSING HISTORY AND TENSILE PROPERTIES OF TITANIUM ALLOY
PANELS SUBJECTED TO VARIOUS CHEMICAL MILLING/HEAT TREATING OPERATIONS

| Specimen No. | Titanium Alloy | Thickness, inches | | Processing History* | TENSILE PROPERTIES | | | H ₂ Content After Proc., ppm |
|--------------|----------------|-------------------|-----------------|---------------------|-----------------------|-----------------------|----------|---|
| | | Original | After Chem-Mill | | F _{tu} , ksi | F _{ty} , ksi | Elong, % | |
| 29A1 | Ti-6-4 ANN | 0.100 | 0.070 | CM, ST, A | 173.0 | 164.8 | 7.0 | - |
| 29A2 | Ti-6-4 ANN | 0.100 | 0.051 | CM, ST, A | 170.2 | 160.8 | 6.0 | - |
| 29B1 | Ti-6-4 ANN | 0.100 | 0.051 | CM, ST, A | 172.1 | 164.3 | 4.0 | - |
| 29B2 | Ti-6-4 ANN | 0.100 | 0.070 | CM, ST, A | 171.9 | 161.5 | 6.0 | - |
| 29L1 | Ti-6-4 ANN | 0.100 | 0.068 | ST, A, CM | 169.2 | 159.0 | 7.9 | - |
| 29L2 | Ti-6-4 ANN | 0.100 | 0.077 | ST, A, CM | 171.4 | 159.7 | 7.5 | 70 |
| 32A1 | Ti-6-4 ST | 0.070 | 0.020 | CM, A | 161.6 | 156.1 | 1.0 | - |
| 32A2 | Ti-6-4 ST | 0.070 | 0.035 | CM, A | 174.0 | 161.9 | 7.0 | - |
| 32B1 | Ti-6-4 ST | 0.070 | 0.021 | CM, A | 167.9 | 155.7 | 9.0 | 88 |
| 32B2 | Ti-6-4 ST | 0.070 | 0.038 | CM, A | 175.3 | 164.1 | 6.0 | - |
| 33C1 | Ti-6-6-2 ANN | 0.065 | 0.013 | CM, ST, A | 167.3 | 162.7 | 1.0 | - |
| 33C2 | Ti-6-6-2 ANN | 0.065 | 0.031 | CM, ST, A | 187.4 | 182.7 | 5.0 | - |
| 33D1 | Ti-6-6-2 ANN | 0.065 | 0.013 | CM, ST, A | 173.1 | 169.2 | 2.0 | - |
| 33D2 | Ti-6-6-2 ANN | 0.065 | 0.032 | CM, ST, A | 185.9 | 181.5 | 5.5 | - |
| 33K1 | Ti-6-6-2 ANN | 0.065 | 0.041 | ST, A, CM | 184.6 | 177.9 | 6.5 | 102 |
| 33K2 | Ti-6-6-2 ANN | 0.065 | 0.030 | ST, A, CM | 182.9 | 173.2 | 6.3 | - |
| 34A1 | Ti-8-1-1 DA | 0.070 | 0.021 | CM, DA | 143.3 | 135.1 | 8.0 | - |
| 34A2 | Ti-8-1-1 DA | 0.070 | 0.042 | CM, DA | 140.2 | 134.4 | 12.0 | 69 |
| 34B1 | Ti-8-1-1 DA | 0.070 | 0.021 | CM, DA | 146.2 | 137.1 | 10.0 | - |
| 34B2 | Ti-8-1-1 DA | 0.070 | 0.042 | CM, DA | 138.8 | 133.3 | 13.0 | 71 |
| 34E1 | Ti-8-1-1 DA | 0.070 | 0.037 | DA, CM | 139.1 | 127.2 | 11.5 | 87 |
| 34E2 | Ti-8-1-1 DA | 0.070 | 0.020 | DA, CM | 137.5 | 126.0 | 13.0 | - |
| 34F1 | Ti-8-1-1 DA | 0.070 | 0.021 | DA, CM | 135.7 | 123.3 | 7.5 | 41 |
| 34F2 | Ti-8-1-1 DA | 0.070 | 0.038 | DA, CM | 150.3 | 135.1 | 10.0 | 46 |

* Symbol definitions are as follows: CM-chem-mill; ST-solution heat treat Ti-6Al-4V for 5 to 15 minutes at 1700°F and then quench in water; Ti-6Al-6V-2Sn for 5 to 15 minutes at 1600°F and then quench in water; A-age Ti-6Al-4V for 4 hours at 1000°F and Ti-6Al-6V-2Sn for 4 hours at 1100°F; DA-duplex anneal for 8 to 10 hours at 1450°F, cool at rate of 50°F per hour to 800°F, air cool to room temperature, reheat to 1425°F, hold for 30 to 60 minutes at 1425°F, and then air cool.

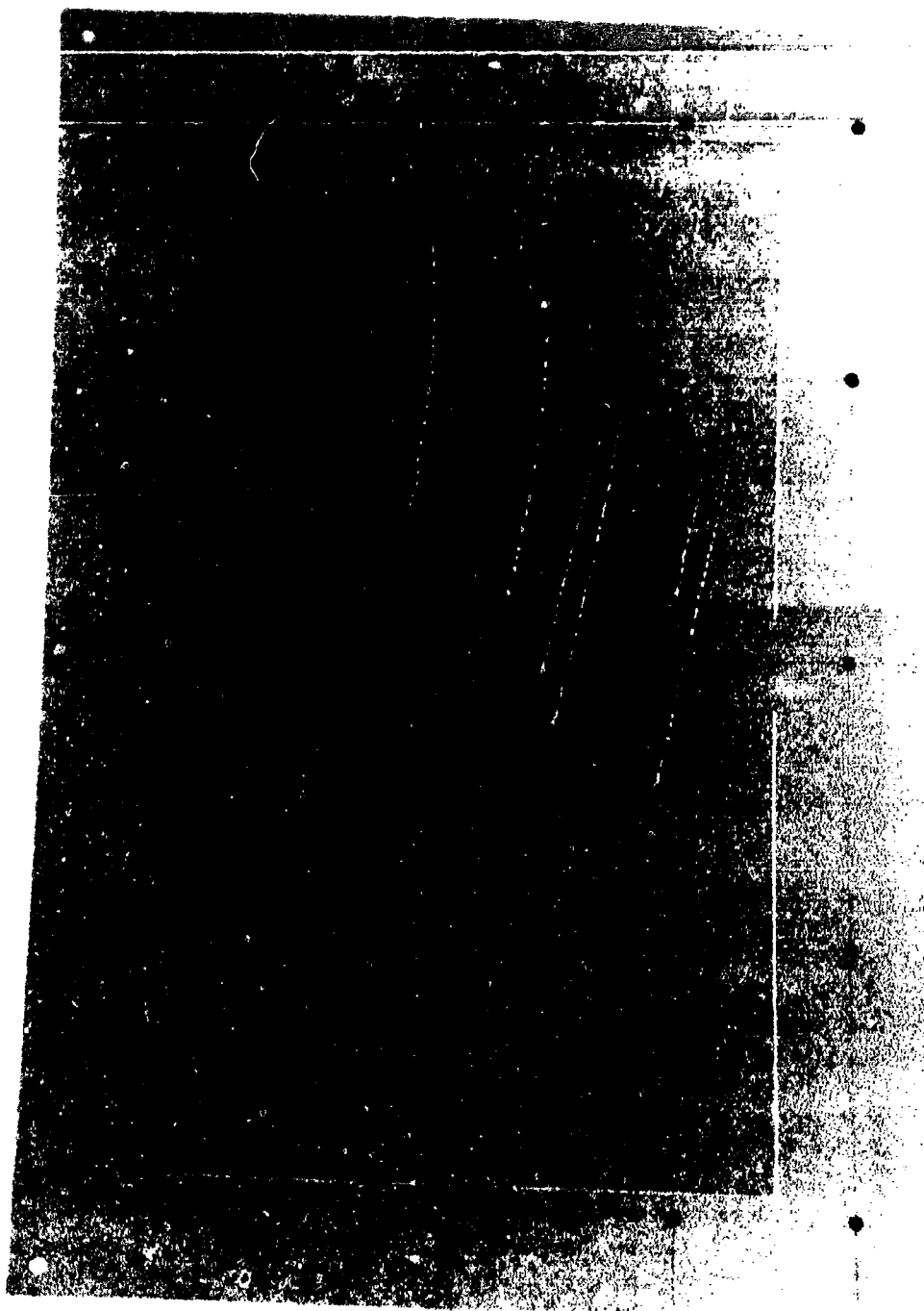


Figure 71 Typical Formed and Chem-Milled Curved Part

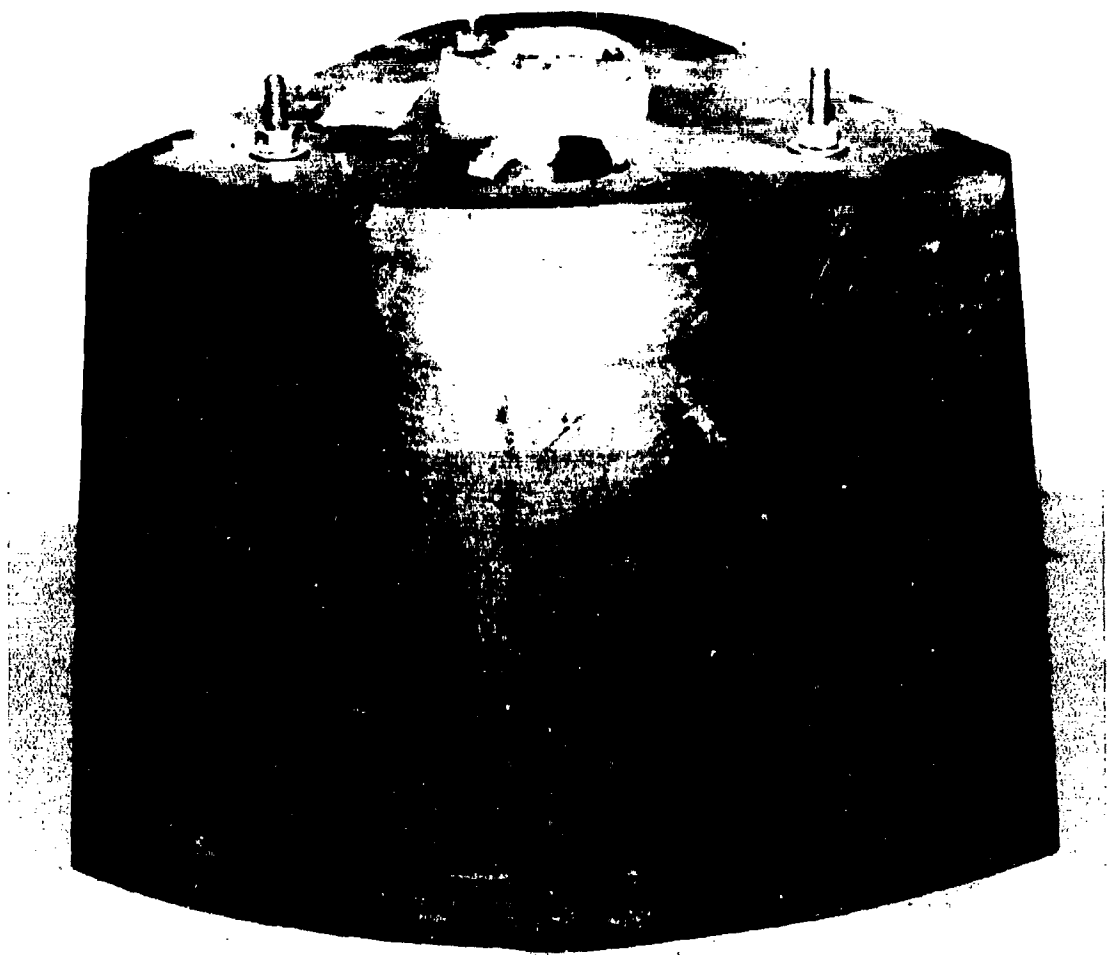


Figure 72 Experimental RDM-2239 Stretch Die

TABLE XXXV
 CHEMICAL MILLING/ROLL FORMING/INCREMENTAL BRAKE
 FORMING METHODIZING OPERATIONS FOR Ti-8Al-1Mo-1V
 TITANIUM ALLOY SHEET

| Test Numbers 14 and 15 | | |
|--|------------|----------------------------|
| Cut 18 x 27-inch blanks | | |
| Drill tooling and hang holes | | |
| Metal stamp part numbers | | |
| Deburr | | |
| Roll form or incrementally brake form | | |
| Inspect and measure contour | | |
| Prepare blanks for chemical milling | | |
| Clean | | |
| Apply maskant and cure at 250°F for 30 minutes | | |
| Scribe maskant | | |
| Etching sequence | | |
| <u>No.</u> | <u>Cut</u> | <u>Remaining Thickness</u> |
| 1 | 0.035 | 0.035 (+0.004, -0.000) |
| Inspect and measure contour | | |

stretch die with an epoxy surface coating that was being used to form F-111A parts was then mounted on the Number 44, 200-ton Hufford stretch press in order to continue the effort to obtain room-temperature, stretch-formed titanium test sheets. An 0.070-inch-thick, Ti-6Al-4V titanium alloy sheet was clamped in the jaws of the press and subjected to a tensile load of 105,000 psi. As the titanium sheet was being wrapped around the die, it failed at the press jaws. The die was severely damaged. Further attempts to stretch-form Ti-6Al-4V titanium alloy sheets were suspended, since a cast Kirksite die would have been required. Failure of the titanium alloy sheet at the press jaws could probably have been prevented by polishing the edges of the jaws to remove minute cracks. The tensile force of 117,000 psi needed to stretch Ti-6Al-4V titanium alloy sheet was not reached. It appears that Ti-6Al-4V titanium alloy sheet can be stretch-formed only by heating it to 1200°F and then wrapping it around cast Kirksite dies.

b. Results

The bending radius of each formed and chem-milled part was calculated using the following equation:

$$R = \frac{B^2}{2D} + \frac{D}{2}$$

where R = radius
 B = one-half the chord length
 D = chord height

Radius measurements after forming and after chem-milling are summarized in Table XXXVI. Analysis of the data indicates that the average change in the part radius due to chem-milling is about equivalent for both roll formed and incrementally brake formed parts. This radius change could be compensated for by overforming the parts. Surface finish of the processed parts ranged from 15 to 20 rms. Line definition was excellent (this is typical of chem-milled Ti-8Al-1Mo-1V titanium alloy sheet).

TABLE XXXVI

RADIUS MEASUREMENTS ON TI-8AL-1MO-1V TITANIUM ALLOY PARTS ROLL FORMED AND INCREMENTALLY
BRAKE FORMED AT ROOM TEMPERATURE AND THEN CHEM-MILLED

| Panel Number | Processing | Radius After Forming, inches | | Radius After Chem-milling, in. | | Change In Radius Due to Chem-Milling, inches | |
|------------------------------------|--|------------------------------|------|--------------------------------|------|--|------|
| | | Indiv. | Avg. | Indiv. | Avg. | Indiv. | Avg. |
| RDM 149814-1A -2A -3A -4A | Roll Formed and Chem-Milled | 72.6 | 66.4 | 95.1 | 82.8 | 22.5 | 16.4 |
| | | 70.2 | | 87.9 | | 17.7 | |
| | | 65.7 | | 80.1 | | 14.4 | |
| | | 57.2 | | 68.1 | | 10.9 | |
| RDM 149815-1A -2A -3A -4A | Incrementally Brake Formed and Chem-Milled | 87.0 | 80.8 | 107.4 | 98.2 | 20.4 | 17.4 |
| | | 86.1 | | 101.5 | | 15.4 | |
| | | 71.1 | | 87.0 | | 15.9 | |
| | | 79.1 | | 96.8 | | 17.7 | |

SECTION IV

AIR POLLUTION TASK

1. APPROACH

The increased application of chemical milling in the aerospace industry, together with the growing concern of federal and local governments with air pollution, make it necessary for air pollution guidelines to be established. A qualitative and quantitative study of air pollution caused by chemical milling was conducted that will be an aid to manufacturers who may be forced into costly innovations by government restrictions.

Conclusions reached during the study are:

- The use of grab sample bottles, gas-tight syringes, polyethylene bags, and absorbing solutions in fritted glass bubblers are effective sampling techniques for gathering air pollutants emitted from chemical milling operations.
- Gas chromatographic analysis can be used to accurately determine the concentration of specific pollutants in the gases emitted from such operations as maskant flow coating, trichloroethylene demasking, and aluminum chemical milling.
- Calorimetric analysis can be used to detect fluorides in gases emitted from titanium chemical milling operations.
- A wide range of air quality or source emission standards for the types of air pollutants emitted from chemical milling operations exists. For example, the states of Connecticut, Kansas, Missouri and Michigan have policies of establishing criteria for specific contaminants only as needs arise, while the states of New York, Tennessee, California, Montana and Texas have the most comprehensive environmental protection laws. Large metropolitan areas such as New York, Los Angeles, Fort Worth and Chicago set emission criteria for specific pollutants and enact local ordinances to enforce these standards. Smaller cities usually rely upon standards set by the states in which they are located or upon Federal Government regulations. They enforce these standards only when the pollutants emitted become a public nuisance or a health hazard.
- Inhalation of such vapors as sodium hydroxide, sodium sulfide, hydrofluoric acid, nitric acid, nitrogen dioxide, chromium trioxide, hydrochloric acid, chlorine, nitrosyl chloride, sulfuric acid, toluene, xylene, and trichloroethylene that can be emitted by certain chemical milling operations are hazardous to health.

Preceding page blank

- The amount of chemical milling pollutants entering the atmosphere can be effectively controlled by using recovery techniques that involve absorption followed by distillation or separation, physical removal techniques that involve wet scrubbing or electrostatic precipitation, or chemical degradation techniques that involve high-temperature incineration of noxious fumes and vapors in the presence of air.

2. STUDY AREAS

The following areas of the air pollution problem as related to chemical milling were studied during the course of this program:

- Sampling Techniques for Pollutants
- Analytical Techniques
- Air Pollution Regulations
- Health Hazards
- Air Pollution Equipment

The geographical locations of some of the major contractors using chemical milling are listed in Table XXXVII. Most of them are situated near large cities where the regulations and effects of air pollution are most stringent. One of the companies listed (Automation Industries of Gardena, California) has already been forced to close its doors as a result of action brought against it by the Los Angeles Air Pollution Control Board.

TABLE XXXVII
GEOGRAPHICAL LOCATION OF MAJOR CHEMICAL MILLING CONTRACTORS
AND SUBCONTRACTORS

| East | Mid-west | Southwest | West |
|--|-------------------------------------|---|--|
| Gruzman, Aircraft Bethpage, N.Y. | McDonnell-Douglas St. Louis, Mo. | General Dynamics Fort Worth, Texas | Automation Ind. Gardenia, Calif. |
| Republic Aviation Farmingdale, N.Y. | Boeing Wichita, Kansas | Texas Aircraft Milling Grand Prairie, Texas | Douglas Aircraft Long Beach, Calif. |
| Twin Industries Buffalo, N.Y. | Beech Aircraft Wichita, Kansas | Anadite Hurst, Texas | Lockheed Burbank, Calif. |
| United Aircraft Hartford, Conn. | Bendix Corp. Kansas City, Kansas | South | Anadite, Inc. South Gate, Calif. |
| | North American Columbus, Ohio | AVCO Nashville, Tenn. | General Dynamics Pomona, Calif. |
| | General Elec. Evandale, Ohio | Chem-Fab, Inc. Hot Springs, Ark. | Boeing Seattle, Wash. |
| | Unichem Detroit, Mich. | Lockheed Marietta, Ga. | Northrop Hawthorne, Calif. |
| | Brooks & Perkins Detroit, Mich. | | Chem-Tronics Los Angeles, Calif. |
| | Goodyear Akron, Ohio | | Ryan Aeronautical San Diego, Calif. |

3. SAMPLING TECHNIQUES

Sampling techniques were established for the major pollutants emitted from chemical milling operations (Table XXXVIII).

TABLE XXXVIII
AIR POLLUTANTS FROM CHEMICAL MILLING PROCESSES

| Chem-mill System | Aluminum | Titanium | Steel | Maskants and Demaskants |
|----------------------------------|--|---|--|---|
| Solution Components | Sodium Hydroxide Sodium Sulphide Sodium Gluconate | Hydrofluoric Acid Hydrofluoric-Nitric Hydrofluoric-Chromic | Nitric Acid Hydrochloric Acid Ferric Chloride | Neoprene - Styrene-Butadiene-polyvinyl Chloride in organic solvents Trichloroethylene demask |
| Typical Chemical Reactions | $Al + NaOH$ $Na_2O \cdot Al_2O_3 + H_2$ +Metallic Sulphides | $Ti + HF \rightarrow TiF_4 + H_2 \uparrow$ | $Fe + HNO_3 + HCl$ $FeCl_3 + NOCl + Cl_2 + H_2O$ | Cross linking or Polymerization during curing |
| Possible Pollutants Emitted | NaOH H_2S | HF $HNO_3 - NO_2$ CrO_3 | HCl HNO_3 Cl_2 $NOCl - NO_2$ | Toluene Xylene Trichloroethylene |
| Analytical Techniques to be Used | Gas Chromatography Wet Analysis Total Alkali by Neutralization | Wet Analysis Total Fluoride Gas Chromatography Total Acidity colorimetry | Total Acidity Wet Analysis Wet Analysis Neutralization Gas Chromatography-Silver Precipitation | Infra-Red Spectrophotometry Mass Spectroscopy |

There are two basic requirements that any sampling technique must meet. It must yield a sample that is representative of the area being sampled. This includes the ability of the technique to not only take the sample but to store the sample until analysis without changing those properties that are being analyzed. The second requirement is that the technique yield a sample that is sufficiently large for the analytical technique being used.

Gas sampling techniques can be divided into two broad categories. The first category consists of those techniques that take an actual physical sample of the gas. These include such devices as evacuated grab sample bottles and gas tight syringes. This type of sampling is ideal for analytical techniques such as gas chromatography which only require a small amount of sample for analysis.

The second category of sampling techniques are those which remove and concentrate that part of the sample which is to be analyzed. These include such techniques as cryogenic trapping of trace compounds and the use of impingers with absorbent solutions. This class of technique is used primarily for trace analysis.

Four techniques were used to take samples for chemical milling air pollution analysis. Three of these techniques were used to take an actual sample while the fourth was used to concentrate the samples for subsequent wet analysis. In air sampling those procedures given in ASTM Method D 1605-60 were followed insofar as was deemed practical.

The simplest sampling technique involves the use of a gas tight syringe with a valve at the tip that can be used to isolate the contents of the syringe. Typical syringes are shown in Figure 73. The large, 500-milliliter syringe is constructed of plexiglass with an aluminum piston and a Viton O-ring. It is used primarily for sampling inorganic gases, since organic vapors tend to be absorbed by the plexiglass giving a subsequent memory effect. The smaller, 20-milliliter syringes are made of glass with a stainless steel plunger and a Teflon O-ring, which are used to take samples of organic vapors for gas chromatographic analysis, are filled by withdrawing the plunger and closing the valve at the tip. These syringes have been used in the past to monitor cabin air in the Lunar Module Program and have been found to be leak-free over a period of days. They are regularly checked to guard against residual contamination.

The second type of sampling technique involves the use of grab sample bottles such as the ones shown in Figure 74. They consist of a glass cylinder with gas and vacuum tight valves at each end. The valves are constructed of glass or Teflon with Teflon stems and Viton O-rings. The valves are readily removable from the bottles and can be disassembled for cleaning. This type of construction minimizes outgassing and residual contamination.

Prior to sampling, the bottles were evacuated and sealed. Once in the sampling area, the valves were opened and the sample sucked into the bottle. The valves were then closed and the sample stored until the analysis was performed. The gas was eventually removed from the bottle by displacement with liquid mercury. This type of sampling yields a 250-milliliter sample which is adequate for any gas chromatographic analysis not requiring concentration techniques.

Third technique involves the use of polyethylene bags to take large-volume gas samples. Infrared analysis, as performed in the laboratory, was performed with 40-meter-path-length gas cells. These cells required a 65-liter sample. To obtain samples of this volume, the apparatus shown in Figure 75 was fabricated. Polyethylene was chosen because it was readily available at low cost and was easy to fabricate. The bags were constructed of polyethylene sleeving in which a bulkhead fitting with silicone rubber gaskets was installed. The sleeving was then heat sealed on both ends to give the desired internal volume.

The bags were inflated with a portable, diaphragm-type air pump designed for 12-volt operation. A single, heavy-duty, six-volt battery will however, provide sufficient pressure for inflation. The inflated bags were returned to the laboratory where the gas was sucked into the evacuated infrared gas cells.

The last type of sampling technique used was the concentration of desired components in an absorbing solution contained in a fritted glass bubbler (Figure 76). Air was drawn through a fritted glass bubbler, needle valve, and flowmeter into a vacuum pump. The needle valve controlled the rate of flow and the flowmeter measured it. The pollutants were trapped by the solution in the



Figure 73 Gas-Tight Syringes

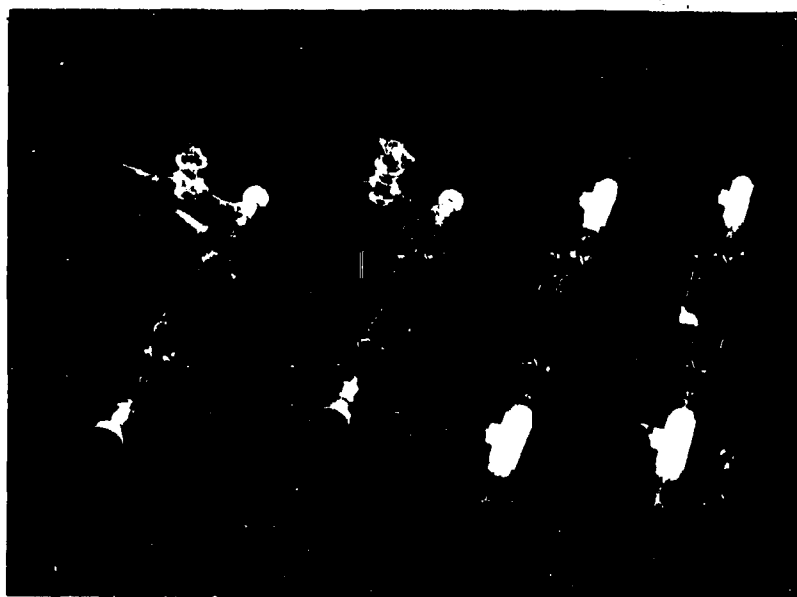


Figure 74 Grab Sample Bottles

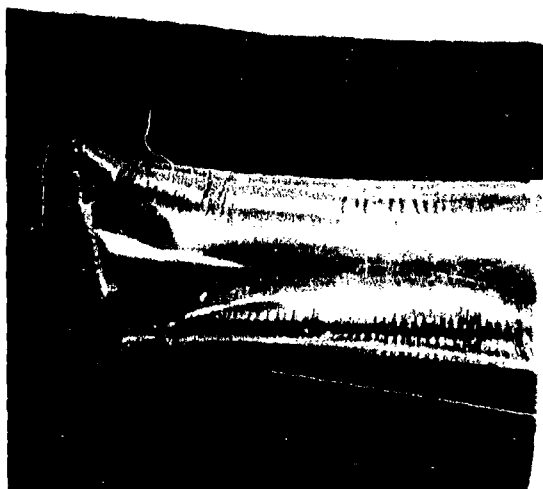


Figure 75 Polyethylene Bag with Portable
Pump and Battery Used to
Obtain Large-Volume Air
Samples

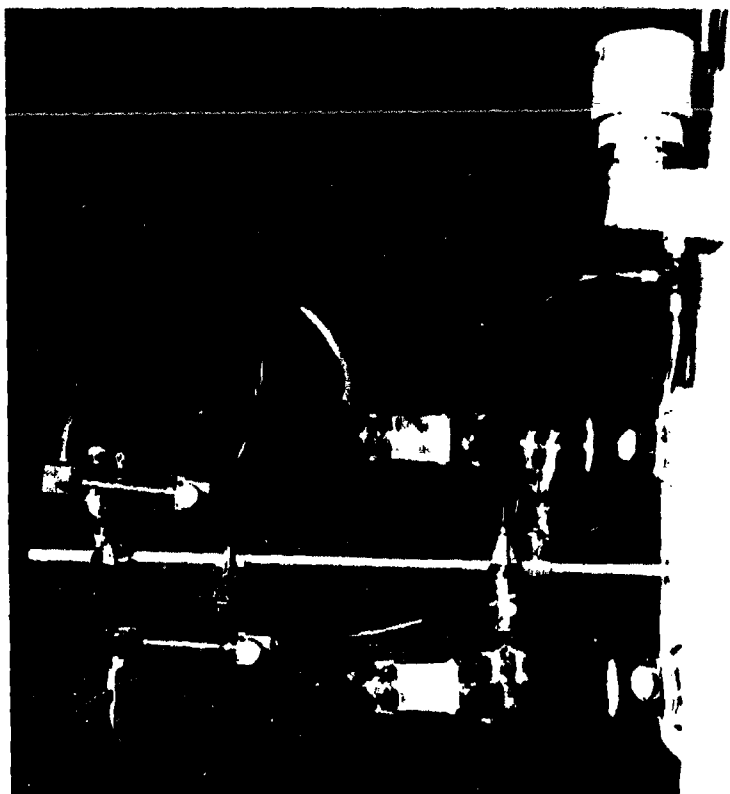


Figure 76 Fritted Glass Bubblers with Flow Meters
and Vacuum Pump

bubbler. The configuration shown allows two different samples to be taken simultaneously, or, alternatively, allows the same sample to be taken twice at different flow rates.

Since the Grumman Chemical Milling Facility has a forced-air ventilation system, the samples were taken directly from the ventilation ducts whenever possible. In the maskant area, the samples were taken directly at the outlet of the ventilation stacks. Thus all values given in this report are for stack air and not for ambient air.

4. ANALYTICAL TECHNIQUES AND RESULTS

a. Maskant Flow Coat Area

Initial qualitative analysis was performed on the exhaust gases from the maskant area with a Perkin-Elmer Model 521 infrared spectrophotometer (Figure 77) and forty-meter-pathlength gas cells. The information provided by this instrument made it possible to set up a gas chromatographic analytical procedure. The organic pollutants in the exhaust gases were found to consist primarily of toluene with a concentration of about 200 parts per million.

The gas chromatographic analysis was performed on a Perkin Elmer Model 800 chromatograph. The operating parameters were as follows:

| | |
|----------------|--|
| Column | - 12 ft X 1/4-inch stainless steel tubing, 5% DC 550 on Chromasorb W. 60-80 mesh |
| Temperature | - 50°C |
| Carrier | - Helium at 80 ml per minute |
| Detector | - Flame Ionization |
| Gas Pressures | - Helium - 54 PSI; Hydrogen - 22 PSI; Air - 38 PSI |
| Attenuation | - X10 |
| Sample Size | - 5 ml |
| Recorder Speed | - One inch per minute |

The samples were taken using 20-ml, gas-tight syringes with a valve at the tip. They were injected into the chromatograph through a gas-sample valve with a 5-ml loop. Toluene, which had a retention time of 12.25 minutes, was the primary pollutant in the exhaust gases. Since the other components were present in only minor amounts, they were merely quantified and expressed in terms of toluene. A typical chromatogram is shown in Figure 78.

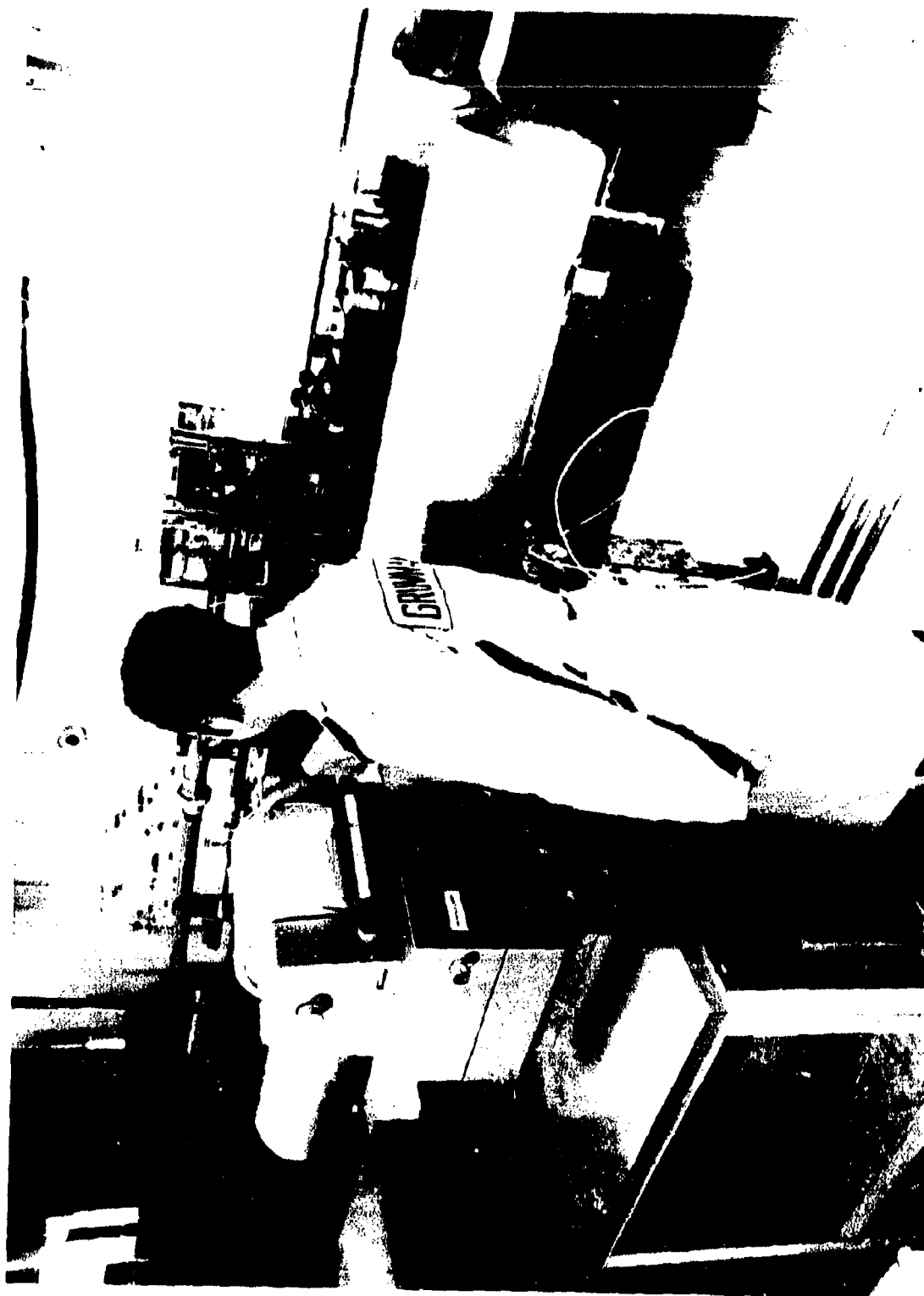
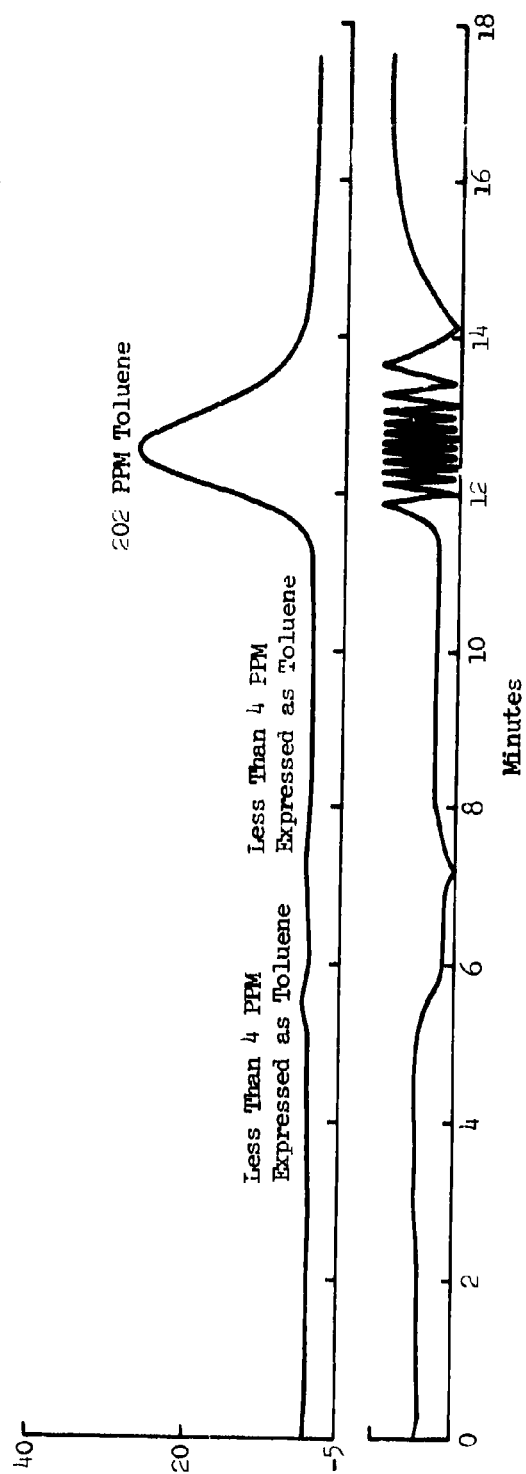


Figure 77 Perkin-Elmer Model 521 Infrared Spectrophotometer



174

Figure 78 Typical Gas Chromatographic Curve for Toluene

The Grumman Chemical Milling Facility includes two, maskant-flow-coat tanks each with its own exhaust system. Twenty samples were taken from these exhaust systems. The average concentration of toluene in the exhaust gases was 165 parts per million. Concentration of the other pollutants combined averaged 17 parts per million expressed as toluene; the largest individual pollutant had an average concentration of 6 parts per million.

Twelve samples were also taken of the exhaust gases from the ovens used to cure the maskant coatings. The only pollutant that was emitted from the curing ovens was toluene at an average concentration of 19 parts per million.

The quantification of toluene can also be done chemically (wet) by the Butanone Method. In this method toluene is nitrated with fuming nitric acid and extracted with methyl ethyl ketone. The color is developed by adding sodium hydroxide. The intensity of the violet color produced is proportional to the amount of toluene present. Standards containing toluene are treated in the same manner for color comparison purposes. The procedure is as follows: Pass twenty ml of air through two ml fuming nitric acid with a specific gravity of 1.50 (Twenty ml should be sufficient for about 125 PPM; for greater sensitivity use a larger sample). Quantitatively transfer the sample to a glass-stopped bottle. The nitrated sample can be held at this point for up to two weeks before finishing the analysis. Put the acid solution in a water bath at 25°- 30°C and titrate slowly with a fifty percent solution of potassium hydroxide until neutralization occurs. Add a slight excess (2-3 drops) of base. Extract the nitrated toluene with ten ml of methyl ethyl ketone at a temperature of 25 - 30°C. Transfer the methyl ethyl ketone fraction to a 100 ml Nessler tube and add 1.5 ml of 50% potassium hydroxide solution. Shake vigorously for several minutes. Let stand for 1-1/2 hours, shaking occasionally while the color develops. Compare the sample to a set of similarly prepared standards.

b. Trichloroethylene Demaskant Tank

Samples were taken of the exhaust gases from the trichloroethylene demaskant tank. The samples were analyzed by gas chromatography using the same analytical conditions used for the maskant pollutant analysis. The exhaust air was found to contain an average of 125 parts per million of trichloroethylene.

A simple wet chemical method for determining trichloroethylene in air is given by Jacobs¹. The air is passed through a bubbler containing alcohol which traps the trichloroethylene vapors. The alcohol is transferred to an alcohol lamp and burned. The decomposition products are trapped in a solution of silver nitrate. The combustion products are decomposed by the water into hydrochloric acid and carbon dioxide. The excess silver nitrate is then titrated with potassium thiocyanate solution. One ml of 0.1N silver nitrate solution is equal to 0.00438 gram of trichloroethylene.

¹ Morris B. Jacobs "Analytical Chemistry of Industrial Poisons, Hazards, and Solvents". Interscience: New York, 1956, pp. 539-544.

c. Aluminum Chemical Milling

The effluent gases from the aluminum chemical milling tanks were checked for alkalinity by passing them through distilled water in a fritted glass bubbler. Flow rates of up to five liters per minute were used for as long as eight hours. No increase in the alkalinity of the water was obtained.

A gas chromatographic procedure was established to analyze the effluent vapors for sulfur compounds. No sulfur compounds were detected at the sensitivity limits of the Perkin-Elmer Model 145D chromatograph which is shown in Figure 79. To go from the lower sensitivity limit of the chromatograph (around 30 parts per million) to the desired level of 0.1 part per million, a concentration technique was used. This was a cryogenic technique in which a known volume of air was passed through a cold-trap and the impurities frozen out. The frozen impurities in the cold trap were then inserted in the carrier gas line and heated to ambient temperature. The impurities vaporized and flowed into the chromatograph where they were analyzed. The cryogenic concentration technique, however, proved impractical due to the large amount of water vapor that was present in the exhaust air carrying the effluent gases from the chemical milling tanks.

Exhaust gases were then analyzed for hydrogen sulfide using the methylene blue method². The gases were bubbled through an alkaline suspension of cadmium hydroxide. The sulfides trapped in the solution were then converted to methylene blue and analyzed colorimetrically. The analytical procedure used was as follows:

Reagents: Amine-Sulfuric Acid Solution. Dissolve 12 grams of N, N-dimethyl-p-phenylenediamine in a cooled mixture of 30 ml of water and 50 ml of concentrated sulfuric acid. Take 25 ml of this solution and dilute to one liter with 1:1 sulfuric acid.

Ferric Chloride Solution. Dissolve 100 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in water to make 100 ml of solution.

Absorption Solution. Add a solution of 4.3 grams of $\text{CuSO}_4 \cdot 8\text{H}_2\text{O}$ in water to a solution of 0.3 gram sodium hydroxide in water and dilute to one liter. Stir before using.

Procedure: Place 75 ml of the absorption solution in a glass bubbler and pass air through the bubbler for 7 hours at a rate of 7.57 cubic feet per hour. Take 25 ml of the absorption solution and add one ml of the amine-sulfuric acid solution followed by one drop of the ferric chloride solution. Let stand for 10 minutes and then dilute to 30 ml. Read absorbance at 670 m μ and compare the absorbance to a standard curve. Prepare a standard curve by reacting known amounts of hydrogen sulfide and plotting their optical density.

The above procedure has a sensitivity of ten parts per billion. Hydrogen sulfide was not detected in the aluminum chemical milling tank effluent gases at this level.

¹ M.B. Jacobs, op. cit. p. 588.

² Frank J. Welcher, ed. "Standard Methods of Chemical Analysis" (New York: Van Nostrand, 1963) PP 634-635.

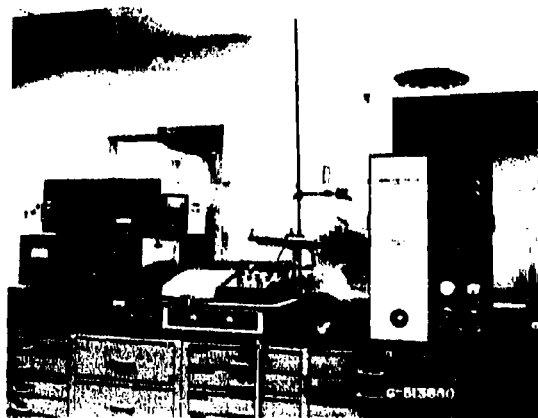


Figure 79 Perkin-Elmer Model 145D Chromatograph

d. Titanium Chemical Milling

Samples were taken of the hydrofluoric acid titanium chemical milling exhaust gases and checked for total acidity. The gases were bubbled through 250 ml of distilled water in a fritted glass bubbler for seven hours at a rate of five cubic feet per hour. Sampling was performed between 8:30 A.M. and 3:30 P.M., the period during which most chemical milling takes place. The solutions were titrated with 0.01N sodium hydroxide. Results ranged from 2.28 to 5.21×10^{-5} grams of hydrogen fluoride per cubic foot of air or 1.55 parts per million.

The analysis of fluorides by electron capture gas chromatography using an ordinary laboratory gas chromatograph has proved unfeasible. Using both gas-liquid and gas-solid techniques, an inability to elute hydrogen fluoride from the columns was experienced. The following liquid phases were used: Kel-F Oil Number 3, Kel-F Oil Number 10, Kel-F grease, Kel-F wax, DC 200, DC 550 and Carbowax 1540. These were coated on Teflon, Kel-F and Chromosorb W supports. In the area of gas-solid chromatography, Porapak Q, Porapak P, Porapak R and Chromosorb 104 were tried.

It is felt that the inability to elute hydrogen fluoride is due to its reacting with the materials used in the construction of the chromatograph. To successfully complete this analysis would require a custom-built chromatograph with all parts of the instrument that are exposed to the sample made from non-corrodible materials such as Monel or Teflon. The entire system could then be passivated by passing hydrogen fluoride through the system to remove any active sites that might exist. Such a passivating process is impossible with an ordinary chromatograph.

The analysis for fluoride was performed colorimetrically using the bleaching action of fluoride ion on a zirconium alizarin lake.¹ The method given in ASTM D1606-60 for inorganic fluoride in the atmosphere is the method of Willard and Winter. This method isolates fluoride from interfering elements by distillation as hydrofluorosilicic acid with a subsequent colorimetric analysis. Since the samples to be analyzed are taken directly from the exhaust duct over the titanium chemical milling tank, it is expected that interfering substances will be negligible compared to the fluoride. The primary interfering substances are alkalinity, aluminum, chloride, orthophosphate, ferric, hexametaphosphate and sulfate.²

The procedure used for analysis is as follows:

- Pass 10 cubic feet of gas through a fritted glass bubbler containing 200 ml of sodium hydroxide solution (5 g. per liter).
- Take an aliquot of 50 ml and bring it to a pH of 1.5 using IN HCL. (This makes the chloride and ferric interferences negligible). Dilute to 100 ml with distilled water.
- Add 5.0 ml of the Alizarin solution (0.075 percent solution of Alizarin Red-S).

¹Snell and Snell. Colorimetric Methods of Analysis, Van Nostrand, New York 1959 pp 638-640.

²ibid

- Add 5.00 ml of the zirconyl acid solution. This solution is prepared as follows: Dissolve 0.354 grams of zirconyl chloride octahydrate in 700 ml distilled water. Add 33.3 ml of concentrated sulfuric acid and 101 ml of concentrated hydrochloric acid stirring as each addition is made. Dilute the mixture to one liter after it has cooled. The solution can be used after standing for one hour.
- Read after 60 ± 2 minutes at 530 mu against a blank of distilled water.

The values obtained are compared to a standard curve that has been prepared from certified sodium fluoride (Figure 80).

The results obtained ranged from 0.001 to 0.003 mg of fluoride per liter of air with an average of 0.0018 mg or 23 parts per million.

e. Nitric Acid Desmutting Tank -

The exhaust gases from the nitric acid desmutting tank were sampled using a fritted glass bubbler containing 250 ml of distilled water. The gases were bubbled through the water for seven hours at a rate of five cubic feet per hour. The samples were titrated with 0.01N sodium hydroxide and total acidity was expressed as grams of nitric acid per cubic foot of air. The results ranged from 5.4 to 13.3×10^{-5} grams of nitric acid per cubic foot of air. The average value was 9.6×10^{-5} grams per cubic foot of air or 1.3 parts per million.

f. Steel Chemical Milling

Since production chemical milling of steel is not currently being performed at Grumman, a small laboratory facility was set up to analyze the pollutants produced. The quantitative data that can be obtained from such a laboratory bath cannot be related to production chemical milling with any degree of accuracy. Therefore, only a qualitative analysis was performed on the vapors given off by the steel chemical milling.

A gas chromatographic analysis was performed using the Perkin-Elmer 154d chromatograph with silica gel columns and a thermal conductivity detector. This revealed the presence of nitrosyl chloride. Subsequent mass spectrometric analysis also showed the presence of small amounts of nitrogen dioxide and hydrogen chloride.

5. AIR POLLUTION REGULATIONS FOR CHEMICAL MILLING CONTAMINANTS

a. Survey of State and Federal Air Pollution Regulations.

Thirty-three air pollution control agencies located in states having major chemical milling contractors were surveyed to obtain information on the following:

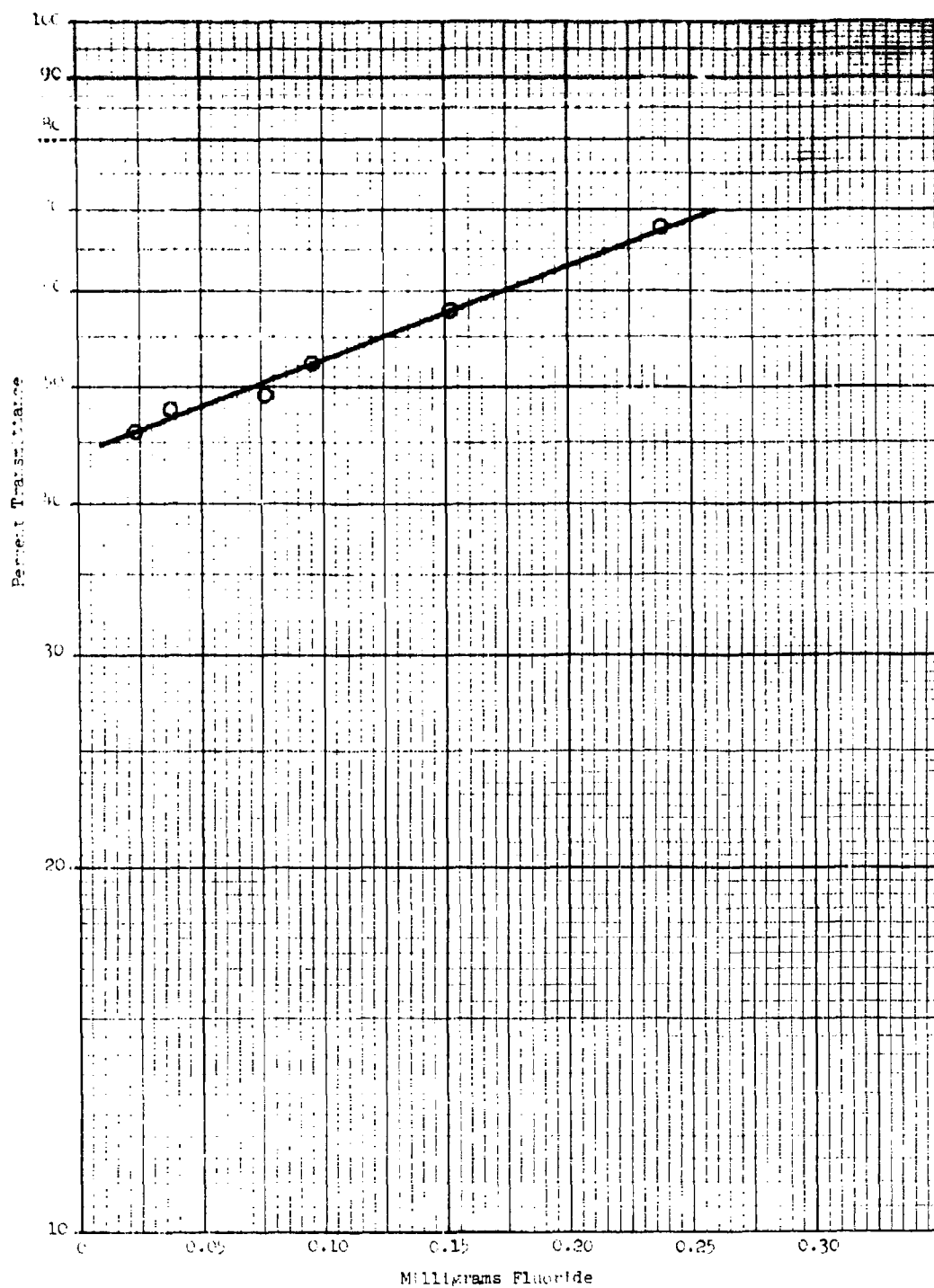


Figure 50 Standard Curve for Colorimetric Fluoride Analysis

- Detection methods applicable to chemical milling pollutants such as organic solvent vapors (xylene, toluene, and chlorinated hydrocarbons) and inorganic vapors and mists of sodium hydroxide, sulfides, fluorides, nitrogen oxides, sulfuric acid, chromic acid, hydrochloric acid, and nitric acid.
- Analytical procedures, preferably instrumental methods.
- Ambient air quality standards established by the agencies for chemical milling pollutants.
- Agency regulations applicable to chemical milling processes.
- Toxicological data for vegetation, animals, and humans.
- Corrosion data for metals and building materials.

The 22 agencies that responded to the survey may be categorized as follows:

- State Agencies 10
- Municipal Agencies 4
- Federal Agencies 4
- County Agencies 4

A surprisingly large number have not set either air quality or source emission standards for the types of chemical pollutants associated with the chemical milling process.

The states of Connecticut, Kansas, Missouri, and Michigan seem to have a policy of establishing criteria for specific contaminants only as the need arises. No research effort has been applied to developing acceptable concentration limits for pollutants associated with the chemical milling process. Should the need arise in the future, their plan is to adopt air quality standards set by the Federal Government or the American Conference of Governmental Industrial Hygienists.

The following municipalities and counties have no standards for organic vapors, sodium hydroxide mists, or acid mists:

Cleveland, Ohio
 Columbus, Ohio
 Kansas City of (Wyandotte County), Kansas
 County of Nassau, New York

The states of New York, Tennessee, California, Montana, and Texas have the most comprehensive environmental protection laws. All five set ambient air quality standards for a wide range of chemical pollutants including those which apply to stack effluents from chemical milling process tanks. Equipment and processes designed to meet these standards would be generally acceptable throughout the nation.

Large metropolitan areas such as New York, Los Angeles, Fort Worth, and Chicago set emission criteria for specific pollutants and enact local ordinances to enforce these standards. Smaller cities, however, rely upon standards set by the states in which they are located or by the Federal Government. They enforce these standards only when they become a public nuisance or a health hazard.

To date, the United States Government has issued Air Quality Criteria Documents for particulate matter and sulfur oxides only. Criteria for carbon monoxide, hydrocarbons, and photochemical oxidants have been written. They will be presented at public hearings throughout the nation over the next few months. Criteria for fluorides, lead, nitrogen oxides, and polynuclear organics will be ready by next year.

Details of replies received from the State and Federal Agencies are as follows:

- California - The state of California Air Resources Board submitted copies of state regulations and ambient air quality standards. The most stringent regulations apply to emissions from motor vehicles. Ambient air quality standards have been established for ozone, carbon monoxide, sulfur dioxide, visibility-reducing particles, hydrogen sulfide and nitrogen dioxide. The Los Angeles County Air Pollution Control District has established Rule 66 which provides for drastic reductions in the emission of industrial hydrocarbons that can enter into photochemical reactions.
- Michigan - The state of Michigan presently has no specific emission limitations or ambient air quality standards for the pollutants emitted by the chemical milling process. They indicated that involvement occurs only when the emissions result in a community nuisance problem.
- Missouri - The Air Conservation Commission of Jefferson City, Missouri, submitted general recommendations for analyzing and controlling process tank pollutants. They stated that state air quality standards will be established after the Federal Government publishes air pollution guidelines. The Saint Louis County Health Department has established ambient air quality standards for sulfur oxides, hydrogen sulfide, oxidants, dustfall and suspended particulates.

- Kansas - At the present time Kansas does not have any air quality standards and regulations. Standards for particulate emissions and sulfur are currently being adopted. Standards for chem-mill pollutants such as hydrogen sulfide, hydrogen fluoride, nitrogen dioxide, sodium hydroxide, chromates and organic solvents are not anticipated in the near future. They will be adopted when the Federal Government establishes criteria and control techniques for them.
- Massachusetts - The state of Massachusetts does not have specific regulations for the pollutants emitted by the chem-milling process. General regulations state that the contaminants should not cause or contribute to a condition of air pollution. Ambient air quality standards have been established for sulfur oxides and particulates only.
- Montana - The Montana State Board of Health has established ambient air quality standards for sulfur dioxide, sulfuric acid, hydrogen sulfide, particulates, lead, beryllium and fluorides. The maximum fluoride levels established by Montana are among the most stringent of all states surveyed.
- New York - The Division of Air Resources of the New York State Department of Health forwarded pertinent sections of New York State air pollution control regulations and a report entitled "The New York State Continuous Air Quality Monitoring System: by D.E. Gower dated 27 January 1969. The Gower report describes the instrumentation and theoretical basis for the air quality monitoring system used through New York State. New York has established five different levels of ambient air quality standards. A Level I area (predominantly agricultural and recreational) would have more stringent requirements than a Level V area (mainly heavy industry). Materials which have extreme toxicity such as beryllium or soluble fluorides would have a maximum allowable concentration. The Bureau of Air Pollution Control for Nassau County in which Grumman operates its chemical milling facility has not established ambient air quality standards but relies on state standards.
- Ohio - The Ohio Air Pollution Control Board has not set ambient air quality standards for chem-mill pollutants. The only standards that have been set up are for sulfur dioxide and particulate matter. The cities of Columbus and Cleveland indicated that they have no air quality standards for the pollutants emitted by the chem-mill process.
- Tennessee - The Tennessee Department of Public Health has established levels of ambient air quality standards based on area classifications similar to those set by New York State. Ambient air quality standards have been set up for dustfall, suspended particulates, soiling index, sulfur dioxide and fluorides.

- Texas - The state of Texas has established comprehensive air pollution regulations and ambient air quality standards. The regulations as in New York and Tennessee are based on the type of land use. Air quality standards have been established for suspended particulates, outdoor burning, sulfur compounds, motor vehicle exhausts, fluorides and beryllium.
- Washington - The Puget Sound Air Pollution Control Agency, Seattle, Washington, does not consider chemical milling to be a serious source of pollution throughout the four counties within its jurisdiction. The Boeing Company does almost all of the chemical milling in this area. All facilities are well ventilated and aqueous vapors and mists are collected with scrubbers. Organic fumes from flow or dip coaters are simply vented to the atmosphere.

No systems have been established yet within the agency for the detection and measurement of pollutants from the chemical milling process. It has no ambient air quality standards that would apply to chemical milling pollutants.

- North Carolina - The National Air Pollution Control Administration, Raleigh, North Carolina recommends standard gas chromatographic techniques utilizing a flame ionization detector for detection, identification and quantification of organic solvent vapors. A hydrocarbon analyzer also equipped with a flame ionization detector can be used in determining the total hydrocarbon content in an air sample. An electron capture detector should be used instead of flame ionization in the gas chromatographic analysis of halogenated hydrocarbons. A fluoride ion electrode is recommended for measuring the fluoride content of a vapor sample collected in a water trap.

Inorganic acid vapors or mists can be collected in water and the resulting solution can be titrated with standard sodium hydroxide solution. An alternate recommendation is to collect the vapors in a standard sodium hydroxide solution and titrate the excess sodium hydroxide with standard hydrochloric or sulfuric acid.

Aqueous solutions of sulfide vapor are best determined turbidimetrically after converting the sulfide to sulfate and precipitating with barium chloride. In a mixture of acids, sulfuric acid can be determined turbidimetrically by precipitating the sulfate with barium chloride. The chloride fraction can be precipitated with a known excess of silver nitrate and the excess silver back-titrated with potassium thiocyanate (Volhard Method).

It is recommended that sodium hydroxide vapors be collected in water and the resulting solution titrated with standard hydrochloric acid solution.

Vague instructions were given for wet chemical analysis of nitrogen oxides. More specific instructions are given for the analysis of sulfur dioxide via spectrophotometry, coulometry and flame photometry.

b. Ambient Air Quality Standards

The ambient air quality standards for possible chem-mill pollutants for the states surveyed are shown in Table XXXIX. The values shown are maximum allowables for extended periods of time. Blank spaces indicate that no standards exist or that standards were not given in the survey replies.

c. Health Hazards

The following are health hazards associated with the inhalation of fumes which can be emitted by the chemical milling process.

- Sodium Hydroxide Mist. Vapors given off by sodium hydroxide solutions can cause ailments ranging from mild irritation of the mucous membranes to severe pneumonitis. Small burns or irritant dermatitis can result if these vapors contact the skin. Inhalation of concentrated mist can damage the upper respiratory tract and lung tissue.
- Sodium Sulfide. In moist air sodium sulfide vapors can produce hydrogen sulfide which is both a tissue irritant and an asphyxiant.
- Sodium Gluconate. This compound is apparently non-toxic.
- Hydrofluoric Acid. Inhalation of hydrofluoric acid vapors may cause ulcers to develop in the upper respiratory tract. Concentration of 50 to 250 parts per million are dangerous even for brief exposures. Concentrations as low as 0.001 to 0.100 part per million by volume are significant air contaminants for plants and animals. Air accumulations of hydrofluoric acid in plant leaves that are subsequently fed to animals cause fluorosis -- a disease that affects bone structure and teeth. Concentrations as low as 20 to 50 parts per billion interfere with plant photosynthesis and produce considerable injury especially in fruit crops.
- Nitric Acid. Nitric acid vapor is highly irritating to the skin and to the mucous membranes of the eyes and the respiratory tract. It is also corrosive to the teeth.
- Nitrogen Dioxide. Nitrogen dioxide gas is highly toxic, causing lung inflammation and subsequently often fatal edema. A concentration of 100 parts per million is dangerous; one of 200 parts per million may be fatal. Nitrogen dioxide is also considered to be a constituent in photochemical reactions with hydrocarbons in the air to produce the irritating particulate matter known as smog. Concentrations in the air as high as 25 parts per million can cause discoloration of plant leaves.

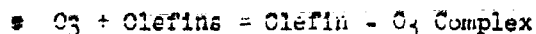
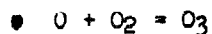
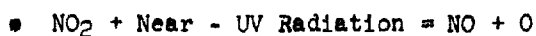
TABLE XXXIX
AMBIENT AIR QUALITY STANDARDS

| State | Pollutant Concentration | | | | |
|----------------------------------|-------------------------|-------------------------------|-----------------|---------------|------------------------|
| | Fluorides | Sulfides | Nitrogen Oxides | Sulfur Oxides | Beryllium |
| California | - | 0.03 ppm** | 0.25 ppm | 0.04 ppm | - |
| Michigan | - | - | - | - | - |
| Kansas | - | - | - | Being Adopted | - |
| Missouri, St. Louis County | - | 0.03 ppm | - | 0.02 ppm | - |
| Mass. | - | - | - | 0.025 ppm | - |
| Montana | 1 ppb* | 0.03 ppm | - | 0.02 ppm | 0.01 UG/M ³ |
| New York | 1 ppb | 0.01 ppm for one hour | - | 0.10 ppm | 0.01 UG/M ³ |
| Ohio | - | - | - | 0.015 ppm | - |
| Tennessee | 1.5 ppb | - | - | 0.10 ppm | - |
| Texas | 1.0 ppb | 0.08 ppm for 30 minutes | - | 0.2 ppm | 0.01 UG/M ³ |
| Washington Puget Sound | - | - | - | 0.1-0.2 ppm | - |

* ppb = parts per billion

** ppm = parts per million

- Chromium Trioxide. Chromium trioxide dust and mist are irritating to the nasal mucous membranes and the respiratory tract and have been associated with hepatitis.
- Hydrochloric Acid. Hydrochloric acid vapors and mists are less toxic to plant and animal life than the previously cited compounds. Concentrations above 10 parts per million, however, can produce choking and possible ulceration of the respiratory tract. Plants can absorb concentrations of hydrochloric acid vapors as high as 10,000 parts per million without damage, whereas absorption of only a few parts per million of fluoride vapors can injure a plant.
- Chlorine. Chlorine gas in concentrations as high as 50 parts per million is dangerous to inhale even for short periods. It is very irritating to the mucous membranes and may cause pulmonary edema.
- Nitrosyl Chloride. Nitrosyl chloride is a gas at room temperature and may be intensely irritating to the eyes, skin, and mucous membranes. Inhalation may cause pulmonary edema and hemorrhaging.
- Sulfuric Acid. Inhalation of sulfuric acid mist causes inflammation of the upper respiratory tract and may lead to chronic bronchitis. It is also irritating to the mucous membranes of the eyes at concentrations as low as 1.5 to 2.5 parts per million.
- Toluene. Few symptoms appear upon exposure to toluene vapor concentrations up to 200 parts per million. At concentrations of 200 to 500, headache, nausea, coordination impairment, and reduced reaction response occur. Rare cases of anemia and enlarged liver have been reported after exposure to toluene vapor concentrations over 50 parts per million.
- Xylene. Xylene vapors produce slight toxic symptoms and little skin irritation.
- Trichloroethylene. The maximum allowable trichloroethylene concentration is 100 parts per million. Inhalation of high concentrations of trichloroethylene can cause narcosis and anesthesia.
- Photochemical Reactions. Some of the environmental pollutants that can be expected from chemical milling operations undergo chemical reactions with atmospheric constituents in the presence of sunlight. The products of these reactions often contribute further hazardous contaminants to the environment. For example, research has indicated that the products of hydrocarbon oxidation in the presence of nitrogen dioxide and sunlight are responsible for eye irritation, decrease in visibility, plant damage, and cracking of rubber goods. Even a fraction of a part per million of nitrogen dioxide can generate a series of reactions that ultimately produce additional pollutants, as follows:



The olefins involved in the above reaction are those that are emitted to the atmosphere by automobile and industrial exhausts. The olefin (or unsaturated hydrocarbon) - ozone complex consists of a variety of decomposition products including free radicals, formaldehyde, higher aldehydes, and polymers of unknown composition. The most important primary photochemical reaction of aldehyde is splitting the molecule into two free radicals. Free radicals are considered to be harmful and irritating to living tissues, since they are capable of removing a hydrogen atom from almost any organic substance upon contact. In the presence of air this type of free radical also reacts to generate peroxides.

Even in the absence of sunlight, nitrosyl chloride may be formed in the atmosphere by the reaction of nitrogen dioxide and moist sodium chloride. Nitrosyl chloride, which strongly absorbs near-ultraviolet radiation, can, in turn, react photochemically to produce nitric oxide and chlorine.

Sulfur dioxide also undergoes photochemical reaction but at a much slower rate than nitrogen dioxide. In the presence of sunlight and oxygen, sulfur dioxide can form sulfur trioxide which, in turn, may react with atmospheric moisture to generate sulfuric acid vapor.

A drastic reduction in the emission of industrial hydrocarbons that can enter into photochemical reactions is the basis for the restrictions of Rule 66 of the Los Angeles County Air Pollution Regulations for organic materials. These regulations are expected to be adopted by the remaining states within the next five to ten years. These regulations should be considered, therefore, in the design of environmental control equipment for chemical milling facilities.

6. AIR POLLUTION CONTROL EQUIPMENT FOR CHEMICAL MILLING OPERATIONS

Manufacturers of air pollution control equipment were surveyed for information concerning the following:

- Equipment to control emissions of chemical milling pollutants
- Regeneration or recovery systems for these pollutants
- Construction materials compatible with chemical milling pollutants

Thirty-one companies responded. A summary of the information received is as follows:

Control of the amount of chemical milling pollutants allowed to enter the atmosphere can be effected by using one or a combination of the following types of equipment:

¹ Air Pollution Handbook, Mogill et al, Chapter 3.

- Recovery
- Physical Removal
- Chemical degradation or incineration

The first two can be used to treat both organic and inorganic pollutants. Chemical degradation equipment, however, is suitable only for hydrocarbons such as solvent vapors from xylene and toluene unless used in combination with recovery or removal techniques.

a. Recovery - This system comprises an adsorption medium followed by distillation or separation techniques.

- Organic solvent vapors such as xylene, toluene halogenated hydrocarbons, and other substituted hydrocarbons can be removed by passing the vapor-laden air through a specially prepared bed of activated carbon. The carbon bed adsorbs the solvent, leaving clean air to be exhausted from the system. Solvent recovery is accomplished by passing steam through the vapor-laden bed. The solvent vapor is carried into a water-cooled condenser where it is liquified. The liquid passes through a separator to remove waste water and leave re-usable solvent. If more than one solvent is present or if the solvent phase is miscible in the water phase, fractional distillation will be necessary to effect separation.
- Inorganic mists such as sulfuric or nitric acid are directed through a series of fiber mist eliminators where condensation to the liquid phase takes place. The liquid is either returned directly to the process tank or subjected to fractional distillation.

A fiber mist eliminator is simply a packed bed of glass or synthetic fibers retained between two concentric screens. Mist particles are collected on the surface of the fibers and become a part of the liquid film that wets the fibers. The liquid on the fibers is moved horizontally through the fiber bed by the drag of the gases and is moved downward by gravity. Liquid drains down the inner screens to the bottom of the element and is returned back to the process via a liquid seal or to a distillation column if more than one acid is present in the mist.

b. Physical Removal - Two widely used methods that fall into this category are wet scrubbing and electrostatic precipitation.

- In the wet scrubber operation, the vapors from the process tank enter a long narrow pipe at the base of the scrubber and flow upward while scrubbing liquid is introduced tangentially to the flow direction of the vapor. The up-flowing gas entrains the scrubbing liquid, simultaneously breaking it down into fine droplets. High scrubbing efficiency is achieved by continuous internal recirculation which creates a dense zone of finely divided liquid droplets in constant agitation providing intimate liquid-gas contact. The liquid-gas stream (with its collected solids, if any) is carried upward where fixed vanes impart a centrifugal

motion that causes the liquor to drop into a collection trough carrying collected solids and soluble gaseous contaminants with it while the cleaned gas continues upward and out of the top of the scrubber. The collected liquor can be re-processed or discarded as waste.

The scrubbing liquid can be water, solutions of acid or base, or an organic solvent-- depending upon the nature of the pollutants involved. For example, when removing the hydrofluoric acid vapors from titanium chem-mill effluent, potassium hydroxide solution would be a wise choice for the scrubbing liquor. The resulting product -- potassium fluoride -- could possibly be used in the precipitation of titanium tetrafluoride from the chem-mill process tank.

- Electrostatic precipitation is a convenient method for removing particulate matter from chemical process effluents.

The gaseous effluent carrying entrained solid or liquid particles is passed between two electrodes generating a unidirectional high-potential field that ionizes the gases. The ions attach themselves to the solid or liquid particles. The charged particles are discharged and collected at the electrodes.

- c. Chemical Degradation - High-temperature incineration in the presence of air represents the most efficient method for effecting the chemical degradation of noxious fumes and vapors into their simplest oxidation products. Where these air pollutants are organic compounds consisting only of carbon, hydrogen and oxygen atoms, the products of complete combustion are carbon dioxide and water vapor--products that can be safely emitted to the environment. However, some organic compounds contain substituents such as chlorine, fluorine, sulfur and nitrogen. In this case, incineration will yield the additional products, hydrogen fluoride, hydrogen chloride, sulfur dioxide and nitrogen oxides -- all of which are health hazards and must be removed from the incinerator effluent before it enters the external environment. This is best accomplished by directing the incineration exhaust system into a wet scrubber/absorber unit.

Catalytic, direct flame, or thermal incineration can be used. In catalytic incineration, the exhaust stream from a chemical process tank is passed over a specially designed precious metal surface where it is completely oxidized at temperatures between 500°F and 700°F. If the exhaust stream temperature is below 500°F, then it must be directed through a heating chamber prior to catalysis; if it is within 500°F - 700°F, then complete oxidation can take place at the catalyst surface without the aid of fuel. In direct flame incineration, complete oxidation of gaseous pollutants is effected by directing the process effluent directly into a flame (usually produced by ignited natural gas) at 1100°F - 1500°F. Fuel costs can be kept to a minimum by passing the hot oxidation products through a suitable number of heat exchangers. The heat recovered can be used to preheat the process effluent prior to its entry into the combustion chamber, thus reducing the amount of fuel required for incineration. In thermal incineration, the principle of oxidation is essentially the same

as that for direct flame incineration except that heat is applied to the process effluent from a source external to the combustion chamber. As a result, a higher combustion temperature is necessary (e.g., where 1100°F - 1500°F is adequate for Direct Flame Incineration, 1500°F - 1800°F is needed for thermal incineration). The relative merits of the three types of incineration are given in Table XXXX.

TABLE XXXX
COMPARISON OF INCINERATION SYSTEMS

| Type of Incineration | Advantage | Disadvantage |
|----------------------|---|---|
| Catalytic | <p>Very low fuel requirement</p> <p>Complete oxidation at low temperature (500 - 700°F)</p> <p>Easily installed in oven exhaust stream</p> <p>Simple maintenance requirements</p> <p>Catalytic elements can be replaced in minutes</p> <p>Heat generated by catalysis can be returned to system for further reduction in fuel costs.</p> | <p>Unsuitable for removing particulate matter</p> <p>Catalytic surface is subject to "Poisoning" by certain chemicals</p> |
| Direct Flame | <p>At a given temperature oxidation is more efficient than in the absence of a flame</p> <p>More efficient at odor removal than catalytic systems</p> <p>System can be designed to achieve 50-60 percent</p> <p>Heat recuperation thus reducing initial fuel requirements by 40-75 percent</p> <p>Elements are not subject to "Poisoning"</p> <p>Controls are easily adjusted to accomodate modification in operating conditions</p> <p>Can handle particulate matter</p> | <p>Higher capital investment than for catalytic incineration</p> |

TABLE XXXX (Continued)

| Type of Incineration | Advantage | Disadvantage |
|----------------------|---|---|
| Thermal | Efficient odor removal Can be designed for excellent heat recuperation Elements not subject to "Poisoning" Can handle particulate matter | Less efficient oxidation capability than direct flame incineration at a given combustion temperature Higher capital investment than for catalytic incineration |

SECTION V

CONCLUSIONS

The following conclusions have been drawn from each of the four tasks of this study:

1. Automated Control of the Titanium Chem-Mill Bath Task

- A new analytical technique, which involves the use of hydrofluoric acid of known normality to reduce metallic interference, was developed that makes it possible to simply and automatically determine the hydrofluoric acid concentration in titanium chem-milling etchants.
- A hydrometric analytical technique was developed to determine the titanium concentration in hydrofluoric acid-based, chem-milling etchants. This technique, which is based on changes in etchant specific gravity caused by varying amounts of dissolved titanium, facilitated the automation of the centrifugal regeneration process for titanium chem-milling etchants.
- An automatic analyzer that was designed and built by Grumman can be effectively used to determine hydrofluoric acid and titanium concentrations and to provide the signals for initiation of the centrifugal titanium removal cycle and addition of make-up hydrofluoric acid.
- The ten percent hydrofluoric acid etchant used to chem-mill titanium can be automatically reclaimed by precipitating the dissolved titanium with potassium fluoride and removing it as potassium fluotitanate sludge in a centrifuge operation.
- An automatic centrifugal regeneration process was developed that not only alleviates the fluoride waste disposal problem but also reclaims 50 percent of the hydrofluoric acid etchant. This process eliminates the need for manual recharging of the etchant tanks, increases production rates, and improves part dimensional tolerances by maintaining etchant bath parameters at optimum levels. Use of the automated, centrifugal regeneration process would reduce waste solution disposal costs by 50 to 65 percent below that for vendor removal costs.

2. Maskant Development Task

- An improved, low-cost, styrene-butadiene maskant was developed that meets all chem-mill maskant requirements, including smoothness and uniformity of coating surface, good scribing and peeling characteristics, and resistance to sodium hydroxide and hydrofluoric acid etchants. The cost to manufacture this maskant is estimated to be about 50 to 65 percent less than that for currently available chem-mill maskants.

- Electrostatic maskant application techniques can be used effectively with the styrene-butadiene maskant developed under this program and with the Turco 522 styrene-butadiene maskant. Electrostatic techniques cannot be used with neoprene maskants such as Organoceram 1-1010, however, because of severe cobwebbing.
- A photoresist technique was developed that can be used to apply chem-mill maskants to titanium substrates. A relatively simple tooling concept was developed to expose to chem-mill maskants internal areas of formed aluminum and titanium alloy skins having bend radii less than two inches.
- The feasibility of using an automated, high-pressure, water-jet cutting system to scribe chem-mill maskants was demonstrated. This system eliminates scratch damage to metal substrates and can be adapted for use with contoured parts.
- Spark testing is an effective technique for detecting pinholes in styrene-butadiene maskants. This technique is not applicable for use with neoprene maskants, however, because of the high conductivity of the maskant material.

3. Methodizing Optimization Task

- The particular order in which titanium sheet metal parts are simultaneously hot formed and solution heat treated, quenched, aged, and chem-milled does not affect the degree of distortion, tensile properties, or hydrogen content of Ti-6Al-4V titanium alloy parts. The processing order does, however, affect tensile properties and hydrogen content of Ti-6Al-6V-2Sn titanium alloy parts. Chemical milling prior to aging excessively increases the hydrogen content of these parts.
- Chemical milling either before or after simultaneous forming and aging does not significantly change the amount of distortion incurred in processing or the tensile properties of Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy sheet metal parts. Chemical milling before simultaneous forming and aging, however, considerably increases the hydrogen content of both titanium alloys over that for as-received stock.
- Since chemical milling of Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V titanium alloy sheet metal parts before one-step hot forming does not cause excessive distortion, degrade tensile properties, or increase hydrogen content, it would be less costly to process titanium parts in this manner because maskant scribing (before chem-milling) and net trimming (after chem-milling) could be done on flat parts.

- Dimensional stability and tensile properties of Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V titanium alloy sheet metal parts are not significantly affected by the particular chem-milling/heat treating sequence used. Tensile ultimate and yield strengths of Ti-6Al-4V and Ti-6Al-6V-2Sn titanium alloy parts are reduced in proportion to the degree to which the parts are chem-milled.
- The change in contour of Ti-8Al-1Mo-1V titanium alloy sheet metal parts caused by chem-milling after room-temperature roll forming or incremental brake forming can be compensated for by overforming the parts a predetermined amount.

4. Air Pollution Task

- The use of grab sample bottles, gas-tight syringes, polyethylene bags, and absorbing solutions in fritted glass bubblers are effective sampling techniques for gathering air pollutants emitted from chemical milling operations.
- Gas chromatographic analysis can be used to accurately determine the concentration of specific pollutants in the gases emitted from such operations as maskant flow coating, trichloroethylene demasking, and aluminum chemical milling.
- Colorimetric analysis can be used to detect fluorides in gases emitted from titanium chemical milling operations.
- A wide range of air quality or source emission standards for the type of air pollutants emitted from chemical milling operations exists. For example, the states of Connecticut, Kansas, Missouri and Michigan have policies of establishing criteria for specific contaminants only as needs arise, while the states of New York, Tennessee, California, Montana and Texas have the most comprehensive environmental protection laws. Large metropolitan areas such as New York, Los Angeles, Fort Worth and Chicago set emission criteria for specific pollutants and enact local ordinances to enforce these standards. Smaller cities usually rely upon standards set by the states in which they are located or upon Federal Government regulations. They enforce these standards only when the pollutants emitted become a public nuisance or a health hazard.
- Inhalation of such vapors as sodium hydroxide, sodium sulfide, hydrofluoric acid, nitric acid, nitrogen dioxide, chromium trioxide, hydrochloric acid, chlorine, nitrosyl chloride, sulfuric acid, toluene, xylene, and trichloroethylene that can be emitted by certain chemical milling operations are hazardous to health.

- The amount of chemical milling pollutants entering the atmosphere can be effectively controlled by using recovery techniques that involve adsorption followed by distillation or separation, physical removal techniques that involve wet scrubbing or electrostatic precipitation, or chemical degradation techniques that involve high-temperature incineration of noxious fumes and vapors in the presence of air.